DEVELOPMENT OF EXPONENTIAL ANSATZE FOR THE DESCRIPTION OF QUANTUM DYNAMICS

A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

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SEPTEMBER 1994

To

my parents

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STATEMENT

I here by declare that the matter embodied in **this** thesis is the result of investigations carried out by me **in the** School of Chemistry, University of Hyderabad, Hyderabad, India under the supervision of Dr. M. Durga Prasad.

In keeping the regular practice **of reporting scientific** observations due acknowledgements have been made whenever the work described is based on the findings of other investigators.

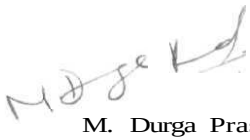
G. Sree Latha

Hyderabad, **G. Sree Latha**

September 1994.

CERTIFICATE

Certified that the work contained in this thesis entitled: 'DEVELOPMENT OF EXPONENTIAL ANSATZE FOR THE DESCRIPTION OF QUANTUM DYNAMICS' has been carried out by G. Sree Latha, under my supervision and the same has not been submitted elsewhere for a degree.



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ACKNOWLEDGEMENTS

With great pleasure I express my gratitude to Dr. M. Durga Prasad who has been training me in this field. His valuable guidance and counselling helped me in bringing this thesis in proper shape.

I express my gratitude to Prof. E. D. Jemmis for his valuable suggestions, encouragement and help throughout my stay here.

I thank the Dean of the school, Prof. P. S. Zacharias and all the faculty members of the school for teaching me many new topics in chemistry.

The encouragement provided by my teachers Mr. M. S. Krishnamachary and Mr. M. Subba Rao is responsible for my adopting the research aptitude.

I take this opportunity to thank Ms. A. Manjula and all my other friends who have provided me homely atmosphere in the campus. I thank my labmates Ms. Madhavi Sastry, Mr. G. Narahari Sastry, Mr. G. Subrahmanian, Mr. G. Naga Srinivas, Mr. B. Kiran and Mr. K. T. Giju for their cooperation.

Financial assistance from the University Grants Commission is gratefully acknowledged. I also thank DST for funding, which provided a sparc station on which most of my calculations were carried out. I wish to thank computer center authorities particularly, the director Dr. Upendra Rao and system analyst Mr. Vinod Kumar for their help when I was doing my computations in CC.

SYNOPSIS

Description of quantum dynamics of molecular systems provides greater insight into the chemically interesting phenomena.[1] Obtaining the dynamics of a system require to solve the time-dependent Schroedinger equation (TDSE)

$$i\hbar\partial\psi/\partial t = H\psi. \quad (1)$$

Here H is the Hamiltonian operator for the system and ψ is the wavefunction. The wavefunction ψ can be expressed as

$$\psi - U_F\phi, \quad (2)$$

where U is the evolution operator and ϕ is the intial state. The TDSE can then be written interms of the evolution operator as

$$i\hbar U_F = HU_F. \quad (3)$$

The evolution operator can be constructed in a number of ways. For example in a perturbative[2,3] fashion where the evolution operator is expanded as a power series or in a nonperturbative way as in Lie- algebraic ' or coupled cluster method.

In this thesis we present a few approaches developed for determining the quantum dynamics. All these approaches invoke exponential form to the evolution operator. In Chapter II we develop degenerate perturbation theories based on an exponential ansatz to obtain the quantum dynamics in finite dimensional vector spaces. This and the non-pertubative approaches to be discussed in latter chapters use the framework of effective Hamiltonian theory.[6] In this approach a group of strongly interacting states are identified as a model space. The wave function is parametrized as

$$\psi = U\phi, \quad (4a)$$

where <p is the projection of ψ on to the model space and U is the time-dependent analogue of the Moller wave operator. These satisfy

$$QHP = 0, \quad (4b)$$

$$i\dot{\phi} = PHP\phi, \quad (4c)$$

$$H = U^{-1}HU - iU^{-1}\dot{U}. \quad (4d)$$

Here P and Q are the projection operators onto the model space M and its complimentary virtual space V respectively.

We posit the wave operator U in a Wei-Norman[3] product form

$$u(t) = \prod_k \exp\,[g_k(t)A_k]. \qquad (5)$$

The operator A are the generators of the Lie algebra to which the Hamiltonian belongs. Based on analysis of the structure of the concerned operator algebra, it is shown that a reduction principle exists. To exhibit it we classify the operator set as follows:

set of excitation operators: $E = \{ X_{vm} = |v\rangle\langle m| \; ; \; v \in V, \; m \in M \}$

set of deexcitation operators: $D = \{ Y = |m\rangle\langle v| \; ; \; v \in V, \; m \in M \}$

set of shift operators: $S = \{ Z = |m\rangle\langle n|, \; W = |u\rangle\langle v| \; ; \; m,n \in M \; ; u,v \in V \}$

It is then demonstrated that when the evolution operator is parametrized as

$$U_F = \exp(X)\exp(Y)\exp(Z+W), \qquad (6)$$

the equations of motion for the generators are decoupled due to the subalgebraic structure present in the operator space. Consequently, the model space wave operator U is given by

$$U = \exp(X)\exp(Y). \qquad (7)$$

The generators X and Y satisfy

$$iX = Q \exp(-X)\, H \exp(X)\, P, \qquad (8a)$$

$$iY = P \exp(-Y)\, [\, \exp(-X)H\exp(X) - iX \,]\, \exp(Y)\, Q. \qquad (8b)$$

These equations are decoupled since X does not depend upon Y.

Expanding X perturbatively we obtain

$$X = \sum_n \lambda^n X_n, \qquad (9a)$$

$$iX_n = H_{QP}\delta_{n1} + H_{QQ}X_{n-1} - X_{n-1}H_{PP} - \sum_{r=1}^{n-2} X_r H_{PQ} X_{n-r-1}, \qquad (9b)$$

where n is the order of perturbation. This approach we term as the similarity transformation based perturbation theory (STP), since in effect, it postulates U = exp(X).

One problem with this approach is that norm may be violated. Exploring the origin of these norm violations, we found that when eq.(4b) is not exactly satisfied, the inverse transform of the

residual term R (=H-H oximate) might not be hermitian and thus might give rise to complex eigenvalues. The component of the wave packet corresponding to such eigenvalues would grow in time leading to norm violations. By defining an R_{OO} such that $R_{OO} = R_{-}^{+}$ and requiring $R = R_{OO}X$ would guarantee that $\bar{H}=H-URU^{-}$ is hermitian. In such a case X must satisfy

$$iX = H_{QP} + (H_{QQ} - R_{QQ})X - XH_{PP} - XH_{PQ}X. \qquad (10)$$

In this case X can not be obtained as a power series. Instead approximations to X are obtained by defining different R_{OO} matrices. We term these approaches as the hermitised similarity transformation based theories (HST).

Another approach which avoid norm violations is obtained by insisting that the full evolution operator underlying wave operator to be unitary. It can be shown by direct substitution that U_F is unitary if Y satisfies the equation

$$Y = -(1+X^{+}X)^{-1}X^{+}. \qquad (11)$$

Thus usage of eq. (8b) with eq. (11) for Y ensures that there is no norm violation. We term this approach as the unitary transformation based perturbation theory (UTP).

We have used the three approaches to follow the dynamics of a harmonically driven Morse oscillator. It appears from these studies that the perturbation theory based on similarity transformation (STP) is adequate atleast for weak coupling or short time dynamics while at longer times the norm violation effects seem to become significant. The nonperturbative approximation (HST) was guaranteed to conserve the norm. The performance of this approximation was quite good. Approximations based on unitary transformation(UTP) do not suffer from norm violation; however, this seems to be achieved at the cost of practically eliminating some of the states from the model space. Its performance is in general worse than an unconstrained similarity transformation based approach.

In chapter III we extend the Lie-algebraic approach to the construction of wave operator in the Fock space. It turns out that this analysis leads to the time-dependent generalization of the multireference coupled cluster methods using an ordinary

exponential ansatz developed earlier in the context of electronic structure theories.[7] There are several sub-algebra sequences present in the operator space of the Fock space, and these can be used to decouple the equations of motion for the various generators. Since the Hamiltonian of a many particle system

$$H = \sum_{i,j} \langle i|h|j\rangle a_i^+ a_j + \sum_{1,J,1,K} \langle ij|v|kl\rangle a_i^+ a_j^+ a_l a_k + \ldots \qquad (12)$$

commutes with the number operator, only those operators which commute with the number operator contribute to U. We note in passing that the complete set of such operators is closed under commutation and hence forms a Lie algebra L. Following Kutzelnigg we classify this operator set as: (i) Set of all Closed operators, C which contain valence operators only. (ii) Set of all operators closed from Below, B. (iii) Set of all operators closed from Above, A. (iv) Set of Open operators, 0 that do not belong to any of the above sets.

We further classify the non-diagonal operators B and A as follows. We define B as the set of B type operator that contain exactly k number of valence and arbitrary number of hole annihilation operators. Similarly we define A as the set of A type operators with exactly k number of valence and arbitrary number of hole creation operators. It is shown that set of operators L = L - B are closed under commutation and thus form Lie algebras. Hence the wave operator is written as

$$U = U_1 U_2 U_3 \ldots \qquad (13a)$$

$$U_k = \exp(S^k), \qquad (13b)$$

$$S^k = \sum_I s_I^k b_I^k \; ; \quad b_I^k \in B_k. \qquad (13c)$$

The working equations are given (analogous to eq.(4)) by

$$Q_k \bar{H}_k P_k = 0, \qquad (13d)$$

$$\bar{H}_k = U_k^{-1} H_{k-1} U_k - i U_k^{-1} \dot{U}_k. \qquad (13e)$$

The model space effective Hamiltonians are just P H P.
It is not convenient to calculate non-energitic properties or transition matrix elements in the above formulation. Since the H are similarity transformations of H, it is possible to calculate such quantities only by obtaining both the left and

right eigenvectors of H. It is desirable to construct H_k that is block diagonal such that it satisfies

$$P_k \bar{H}_k Q_k = 0. \quad (14a)$$

$$U_k' = \exp(\Sigma^k) \quad (14b)$$

$$\Sigma^k = \sum \sigma_I^k a_I^k \; ; \; a_I^k \in A_k, \quad (14c)$$

The final wave operator has the form

$$U = U_0 U_0' U_1 U_1' U_2 U_2' \ldots U_n U_n' \quad (15)$$

For zero valence problem, this operator reduces to the form suggested by Arponen in his development of the extended coupled cluster method. The final H is of block diagonal form. Hence its left and right eigenvectors are confined to the model space. These can be used along with the effective operators to evaluate transition matrix elements.

In Chapter IV we test the applicability of the multireference time dependent coupled cluster method (MRTDCCM) developed in the Chapter III for describing the intramolecular vibrational relaxation (IVR) process in two model systems. Our first system is a simple hydrocarbon chain model studied earlier by Hutchinson et al.[11] The initial conditions are defined such that the CH oscillator is in one of its excited eigenstates at t = 0. The Hamiltonian of the system is taken to be

$$H = H_0 + V, \quad (16a)$$

$$H_0 = p_{CH}^2 / 2\mu_{CH} + D\,(1 - \exp(-\alpha q_{CH}))^2 + 1/2 \sum_{i=1}^{\tilde{}} (p_i^2 + \Omega_i^2 q_i^2), \quad (16b)$$

$$V = -1/m_C \sum_{i=1}^{4} L_{1i}^{-1} p_{CH} p_i, \quad (16c)$$

where i is the harmonic mode index. D and a are the Morse parameters for the CH bond. The eigen functions of H are the oscillator product states $|m>|n>|n>|n>|n>$, where m is the quantum number of the Morse oscillator and n is the quantum number of the ith harmonic oscillator. We have studied dynamics for two initial conditions with quantum number m = 4 and 5 at t=0. Several near degeneracies exist among the zeroth order

states of the system due to the CH bond anharmonicity. Our model space consists of all the states $\{ |m,0,0,0,0\rangle; 0 \le m \le M \}$. The necessary sets of operators for this model space are:

$$C_0 = \{ 1 \}$$

$$C_1 = \{ a^{1+}_m a^1_n; \quad 0 \le m,n \le M \}$$

$$B_0 = \{ a^{1+}_{v_i} a^1_0, \; a^{1+}_{v_i} a^1_0 a^{j+}_{v_j} a^j_0, \ldots; \quad 0 \le v_i, v_j \le N_i, \; 2 \le i,j \le 5 \}$$

$$B_1 = \{ a^{1+}_m a^1_n a^{1+}_{v_i} a^1_0, \ldots; \quad 0 \le v_i \le N_i, \; 2 \le i \le 5, \; 0 \le m,n \le M \}.$$

Here first mode (i=l) is Morse oscillator and 2 to 5 are harmonic oscillator modes.

The closed operators belonging to C and C contribute to the model space effective Hamiltonian. The open from below operators B and B contribute to the cluster operator that genrates U. U can now be written as

$$U = U_0 U_1, \tag{17a}$$

The governing equations for S° are decoupled from those of S^1 due to subsystem embedding condition. It can be shown that U =1 for this Hamiltonian. Hence

$$U = U_1. \tag{17b}$$

With our choice of the model space and the operator set, the cluster operator S^1 consists of operators that excite the bath modes and simultaneously cause scatterings among the Morse states:

$$S^1 = S^1_2 + S^1_3 + \ldots \tag{18a}$$

$$S^1_2 = \sum_{i,p_i} \langle m \; p_i \; |S_2| \; n \; h_i \rangle \; a^{1+}_m \; a^{i+}_{p_i} \; a^1_n \; a^i_{h_i}. \tag{18b}$$

We have calculated the survival probability of the initial state and the energy of the Morse mode as a function of time.

We also studied the utility of a mixed representation in which we treat all the bath harmonic oscillators in terms of boson ladder operators and the Morse oscillator in the basis set representation. Again only U is required for obtaining the dynamics. The cluster operator S^1 in this representation is

$$S^1 = S_1^1 + S_2^1 + \ldots \quad (19a)$$

$$S_1^1 = \sum_{m,n} S_{mn\alpha}^1 \, a_m^{1+} a_n^1 \, b_\alpha^+ , \quad (19b)$$

etc. Here m, n are the Morse oscillator basis functions.

In the second application, we consider the haydrocarbon chain discussed above interacting with the radiation field via the term V

$$V' = A \, q_{CH} \cos(w_r t), \quad (20)$$

where A is the field strength and w is the frequency of the radiation field. In our calculations we have set equal w such that the initial state |0,0,0,0,0> is in 4:4 resonance with the final state |4,0,0,0,0>. The calculations are carried out in the basis set representation and the cluster expansion is truncated after S approximation.

For system-I, for the initial conditions that we have studied, a rapid and irreversible decay is observed due to the presence of several overlapping non-linear resonances. The MRTDCCM approach with ordinary exp(S) ansatz is able to provide an adequate description of IVR at two body level since it simulates the 3, 4 body excitations as products of S^1 operator. Beyond about 4 vibrational periods the inherent weakness of the method i.e. the development of the intruder states with the complex eigenvalues mars its performance. If the model space is chosen judiciously so as to include all the strongly interacting states, its performance is expected to improve. The normally ordered exp(S) ansatz does not suffer from the intruder state problem but it is not converged in the basis and requires the inclusion of higher rank operators just as in configuration interaction (CI) method. The boson representation reproduced the survival probabilities to a better extent for longer times than the basis set representation because it effectively includes the full basis of the harmonic oscillator modes. In the second system within the time scale of our study the many body interactions do not play a major role and the ordinary MRTDCCM is no better than the normally ordered MRTDCCM.

In Chapter V we study the applicability of TDCCM to study

the electronic-vibrational energy transfer in systems containing **nonadiabatically** coupled potential energy surfaces and developed TDCCM in a **dynamical** basis generated by the TDSCF aproach for the problem. We model our systems such that only two electronic states belonging to different irreducible representations and **n-vibrational** modes are relavent for the dynamics.[1] The **Hamiltonian** for the two state n-mode system is taken to be

$$H = \sum |e_i\rangle (\varepsilon_i + H_i) \langle e_i| + V_c, \tag{21a}$$

$$H_i = \sum_n h_{in} = \sum_n (\omega_n (p_n^2 + q_n^2)/2 + k_{in} q_n), \tag{21b}$$

$$V_c = |e_1\rangle \sum_c (\lambda_c q_c) \langle e_2| + h.c., \tag{21c}$$

where i is the electronic state and n represents the vibrational mode. In this nonadiabatic problem the coupling mode and the electronic degrees of freedom interact strongly. So we treat them as a single subsystem.[13] The resulting Hamiltonian for the system can then be written as

$$H = H^{ec} + H^{t}. \tag{22}$$

Here H is the Hamiltonian corresponding to coupling mode electronic degree subsystem and H is the Hamiltonian for the tuning modes. We have taken the single reference CCM reference function ϕ by

$$\phi_0 = \phi_{ec}^{(0)}(r_e, q_c) \prod_t \phi_t^{(0)}(q_t) .$$

Since **this** two state and n-mode nonadiabatic system contains zero valence and arbitrary number of hole creation operators only C **and B** type operators sets are necessary for obtaining the dynamics in this model. The evolution operator can then be written as

$$U = U_0, \tag{24a}$$

$$U_0 = \exp(S^0); \; S^0 \epsilon B_0 \cup C_0. \tag{24b}$$

The cluster operator S° is expanded as

$$S^0 = S_0^0 + S_1^0 + S_2^0 + \ldots \tag{24c}$$

$$S_0^0 = s_0^0 . 1, \tag{24d}$$

$$S_1^0 = \sum_{i,m} s_1^0 a_m^{i\,+} a_0^i, \tag{24e}$$

etc. The working equations became stiff in a very short period of time and we could not get enough information to obtain the sufficiently resolved spectra.

In the above static basis set expansion approach the intruder states with the complex eigenvalues become important even in short time dynamics. This problem can be circumvented by using the dynamical basis sets in terms of which reference state has significant overlap with the exact wavefunction over longer periods. We specifically use the basis functions generated by TDSCF[13] approach to perform TDCCM calculation for this problem. The function ϕ in the dynamical basis is written as

$$\phi^{(t)} = \prod_t \phi_t^{(t)}(q_t)\phi_{ec}^{(t)}(r_e, q_c) \qquad (25)$$

Here the functions ϕ and $<p$ are determined by TDSCF method. We now invoke TDCCM ansatz. We approximate the one body cluster operator S° to zero because the TDSCF incorporates these effects.

Autocorrelation functions and spectra are calculated for four model systems: (1) 3-mode ehtylene cation[14] second band, (2) 3-mode pyrazine[15] S surface, (3) 4-mode pyrazine[16] S_2 surface, (4) 24-mode pyrazine[16] S_2 surface and are compared with TDSCF method. The equations in this formalism are not stiff at least over the time period of our study. In all the calculations TDCCM approach has shown significant improvement over TDSCF method.

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CHAPTER I

INTRODUCTION

Interpretation of properties of matter is a challenging field of fundamental interest for scientists. The analysis of macroscopic properties of a bulk system requires the understanding dynamical behaviour of the system at the molecular level i.e. molecular dynamics of the system.[1] The substantial development in instrumentation and spectroscopic techniques has created a need for the development of theoretical methods to provide proper description of molecular dynamics. There are many theoretical methods developed till date for molecular dynamics studies. The standard approaches for obtaining such dynamics are (a) classical trajectory methods (b) semi-classical methods and (c) quantum mechanical methods.

Quantum effects such as the influence of zero point motion and the tunneling effect etc. are extremely important for certain dynamical events at the molecular level. Classical and **semiclassical** methods cannot always provide a proper description of such processes. In this context, several quantum mechanical approaches have been developed for describing the dynamics of many particle systems.[2] One can obtain the quantum dynamics in two ways: one is the time-independent approach and the other time-dependent approach. Basically the **time-independent** or the time-dependent Schroedinger equation is solved respectively in the time-independent and time-dependent approaches.

The time-independent approaches[4] require all **the** eigenvalues and **eigenstates** of the **hamiltonian** of the system considered and hence involve the construction and diagonalisation of large matrices. In certain conditions the time-dependent approaches are computationally faster. They are initial value

problems and so are often easier to implement. They are becoming increasingly popular due to their applicability to non-fully resolved experiments such as low resolution absorption, Raman spectroscopy and scattering. The other important processes in which the time-dependent approaches are applicable in obtaining the quantum dynamics are transition state spectroscopy, intramolecular energy transfer and collision dynamics in molecular beams. Noteworthy among the advantages these approaches offer are the ability to treat high level densities and the intuitive picture they provide for the physical process under study. Similarly description of externally driven systems requires the solution of time dependent Schroedinger equation. In relevance to our work a brief review on time-dependent approaches that are currently in vogue is presented here.

In the TD approaches the hamiltonian H determines the time evolution of the system according to the Time-Dependent Schroedinger Equation (TDSE),

$$i\hbar\, a\,\psi\ /a\ t\ =\ H\,\psi. \qquad (1.0.1)$$

The time evolution of the wave function can also be represented as

$$\psi(t)\ =\ U(t,t_0)\ \psi(t_0), \qquad (1.0.2)$$

$$U(t_0,t_0)\ =\ 1, \qquad (1.0.3)$$

where U(t,t) is the evolution operator which describes the

evolution of one vector in the Hilbert space into others. Substituting these equations in TDSE gives

$$ih\,\partial\, U(t,t_0)\,/\partial\, t \;=\; H\, U(t,t_0). \qquad \textbf{(1.0.4)}$$

Obtaining the dynamics requires the solution of either eq.(1.0.1) or eq.(1.0.4). Several methods have been discussed in literature for the purpose. They can be classified broadly as (1) perturbative, (2) variational and (3) nonperturbative methods.

1.1 PERTURBATIVE APPROACHES

In the perturbative approaches H is generally written as

$$H \;=\; H_0 \;+\; V(t), \qquad \textbf{(1.1.1)}$$

where H is part of the hamiltonian whose solutions are known and V(t) is the perturbation.

In the time-dependent perturbative methods, the evolution operator form of TDSE (eq.(1.0.4)) is considered and U is expanded as a power series in V. Depending on the construction of U(t,t) these approaches can be subdivided into: (1) Dyson perturbation theory,[6,7] (2) exponential perturbation theory,[8-16] (3) degenerate perturbation theory.[17-19] In addition, it is possible to use either stationary basis or dynamical basis[20,21] to define the Hilbert space of interest.

1.1.1 Dyson Perturbation Theory:

Using the solutions of H the wave function and the operators of the Hilbert space can be written down in a interaction picture frame. In the interaction picture the wave function is written as $\exp(-iH_0 t)\,\psi(t)$ and the interaction hamiltonian is written as

$$H_I = \exp(iH_0 t)\, V(t)\, \exp(-iH_0 t). \qquad (1.1.2)$$

In this picture the evolution operator is denoted by U . The TDSE in this representation is

$$ih\, \partial U_I(t,t_0) / \partial t = H_I\, U_I(t,t_0). \qquad (1.1.3)$$

U is now expanded as a power series of H

$$U_I(t,t_0) = U_I^{(0)}(t,t_0) + \sum_{i=1}^{\infty} U_I^{(i)}(t,t_0), \qquad (1.1.4a)$$

$$U_I^{(0)}(t,t_0) = 1. \qquad (1.1.4b)$$

This expansion is termed as Feynman-Dyson expansion. The second term onwards correspond to first, second and so on ordered solutions of eq.(1.1.3). The power series in H (t) converge more rapidly the closer $U^{(0)}(t,t)$ is to $U(t,t)$. The calculation of higher order expansions become increasingly complicated and so one is constrained to stop at the lower order approximations.

This conventional perturbation theory has certain practical disadvantages. For example any truncated expansion to the evolution operator is not unitary and this method is reliable only for small times and weak perturbations. Alternative expansions to the evolution operator which produce unitary approximations to V at the truncated levels are thus preferable.

1.1.2 Exponential Perturbation Theory:

Exponential form to the evolution operator is very convenient to define unitary approximations. Two such expansions which posit an exponential form to the evolution operator are the Magnus[8,9] and Fer[9,16] expansions. Of these two expansions Magnus expansion have been extensively applied.

In Magnus expansion[8,9] $U(t,t_0)$ is expanded as

$$U_I(t,t_0) = \exp [A(t,t_0)], \qquad (1.1.5a)$$

$$A(t,t_0) = \sum_{i=1}^{\infty} \lambda^n A_i(t,t_0), \qquad (1.1.5b)$$

The operator A is chosen as anti-hermitian to produce unitary approximation to U . In this expansion A is an infinite series in which the n th term is a sum of integrals of n-fold multiple commutators of H (t) . For example, the first few terms in A are[9]

$$A_1(t,t_0) = -i \int_{t_0}^{t} dt' H(t'), \qquad (1.1.5c)$$

$$A_2(t,t_0) = 1/2 \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1 [H(t_1),H(t_2)], \qquad (1.1.5d)$$

The Magnus expansion can be reduced to a simplified form when the hamiltonian is expressible in terms of the generators G_i of a finite dimensional Lie algebra L.

$$H_I = \sum_{i=1}^{n} h_i(t)\, G_i, \qquad (1.1.6a)$$

$$[G_i, G_j] = \sum_{k} C_{ij}^{k}\, G_k; \quad G_i, G_j, G_k \in L. \qquad (1.1.6b)$$

In this case the exponent A must also be a linear combination of the Lie elements,

$$A(t,t_0) = \sum_{i=1}^{n} A_i(t,t_0) G_i. \qquad (1.1.7)$$

By applying closure property of the generators of Lie algebra and simplifying, the Magnus expansion reduces into a set of nonlinear differential equations in A . In the Fer expansion[9,16] the evolution operator is written in the form

$$U(t,t_0) = \exp(\lambda S_1)\exp(\lambda^2 S_2)\exp(\lambda^3 S_3)\ldots \qquad (1.1.8)$$

The recursive solutions to S are obtained as in Magnus expansion.

There are several applications of Magnus expansion. Important among them are applications to NMR and optical spectroscopy.[10] Scheck et al.[11] and others applied this theory to high order molecular multi-photon excitation and noted that Magnus

expansion provides a practical method to go beyond the Rotating Wave Approximation (RWA). Cross[12] has studied rotationally inelastic scattering using second order Magnus expansion with a classical correction to the inelastic part and the results are in good agreement with the accurate results.

Several authors have discussed the convergence of Magnus expansion.[8,13] Pechukas and Light[8''] discussed about the convergence of Magnus expansion in the impulse limit. The first term in the Magnus expansion suffices provided the perturbation is infinitely brief and infinitely strong. Applications to harmonically driven two-level system, two level system in a rotating field and a multiple pulse model by Salzman[13] showed that Magnus expansion in Schroedinger picture diverges. Several of the applications in interaction picture faced no divergence problems.[13] The main drawbacks of the Magnus expansion are the equations for the generators A obtained from eg.(1.1.3) are infinite order polynomials. Under certain exotic conditions, the existence of the solution itself is doubtful.[8(a),14]

1.1.3 Degenerate Perturbation Theory:

An inherent weakness of any pertubation expansion is that when two or more states interact strongly, the pertubation expansion either diverges or converge very slowly to be of any practical use. To deal with such situations quasi-degenerate pertubation theories have been developed. In these theories the interaction in the subspace M spanned by the strongly interacting states (called the model space) is treated exactly. The (weaker)

couplings between the model space and its complimentary virtual space are treated by pertubation theory. To this end a wave operator Ω is defined such that

$$UP = \Omega U_M, \tag{1.1.9}$$

$$U_M = PUP. \tag{1.1.10}$$

Thus

$$\Omega = UP\,(PUP)^{-1}. \tag{1.1.11}$$

Here P is the projection operator onto the model space M. The wave operator is now obtained from pertubation theory

$$\Omega = 1 + \sum_{n=1} \lambda^n \Omega^{(n)} \tag{1.1.12}$$

and an effective hamiltonian H_{ff} is posited to generate the model space dynamics.

$$i\dot{U}_M = H_{eff} U_M. \tag{1.1.12}$$

Jolicard and co workers ' discussed an iterative scheme to calculate fi and H -- in a self consistent manner. Jolicard[18] used this approach to follow the dynamics of a triatomic molecule in intense monochromatic fields and found that the method is dependable.

Another perturbation approach which is used in the study of dynamical evolution is the Generalized Van Vleck (GVV) perturbation theory.[19] It is generally used along with the Many Mode Floquet theory (MMFT)[19(e),(f)]. MMFT converts an

N-level time-dependent system exposed to polychromatic fields into an infinite dimensional time-independent eigenvalue problem. GVV perturbation theory is then used to Block diagonalise this time-independent hamiltonian[19(g)] such that the coupling between the model space and the remainder of the configuration space is reduced to a desired order. The model space hamiltonian can then be considered as a total effective hamiltonian to approximately solve a set of nearly degenerate states. GW perturbation method can also be used along with the Floquet Liouville Super Matrix (FLSM) approach for determining the quantum dynamics.

1.1.4. Perturbation theory in dynamical basis sets:

The studies described above use eigenfunctions of some suitably chosen operator (the unperturbed hamiltonian) as the basis of the Hilbert space. The convergence of the pertubation theory depends critically on the choice of the basis set. Several authors have considered the use of dynamical basis functions to represent the Hilbert space in recent years. These functions change in time and are tailored to follow (to the extent possible) the exact wave packet in time. The details of the construction of such dynamical basis functions is discussed later in the context of the variational approaches.

Recamier et al.[20] described the time evolution of linearly driven parametric oscillators using an operator algebra. They make use of a dynamical basis set expansion and the vibration-vibration coupling is treated pertubatively.

In recent years another method which employs

perturbative treatment is the Perturbation Corrected Time-Dependent Self-Consistent Field (PCTDSCF)[21] method. This method when applied to He + H_2 vibrationally inelastic collisions produced results in good agreement with the exact results.

1.2. VARIATIONAL APPROACHES

In the variational approaches, the wave packet is expanded in terms of a set of basis functions

$$\psi = \sum_n C_n(t)\, \chi_n. \tag{1.2.1}$$

The coefficients C_n are obtained from the Frenkel variational principle and satisfy

$$i\dot{C} = (H - H_0)C, \tag{1.2.2a}$$

$$i\dot{\chi}_n = H_0\chi_n. \tag{1.2.2b}$$

One can carry out the expansion in eg. (1.2.1) in terms of either stationary basis functions whose probability distribution remains constant in time

$$d/dt(\chi_n^* \chi_n) = 0 \tag{1.2.3}$$

or in terms of dynamical basis functions where eq.(1.2.3) does not hold. The major questions to be addressed in this approach are regarding the representation to be used for the basis vectors and the time propagation. These are discussed below.

1.2.1. Stationary Basis Set Methods:

In these methods the expansion functions x are assumed to be either the solutions of time-independent hamiltonian or some functions which do not vary with time. One of the general approaches for the construction of basis is the variational matrix representation method. In this x are expanded in terms of an orthonormal basis of N functions and the variational coefficients are determined by diagonalisation. The effort in this Variational Basis Representation (VBR) depends on the complexity of the hamiltonian matrix evaluation and the size of the matrix representation required for adequate accuracy. In general the size of the matrix is large demanding high computational effort even for slightly larger systems.

Light and co workers suggested a different representation known as Discrete Variable Representation (DVR)[22]. In this representation the approximate solutions are expressed at a well defined set of coordinate points in a grid space:

$$\chi_n(q) = \sum a_n g_n(q), \qquad (1.2.4)$$

where $g_n(q)$ are chosen from an orthogonal basis. One way is to use Gaussian Quadrature points of orthogonal polynomials:

$$g_n(q) = w_\alpha(q) p_n(q), \qquad (1.2.5)$$

where q are quadrature points, w (q) is a weight function and $P_n(q)$ is an orthogonal polynomial. The orthogonality and

completeness relations are given by

$$\sum_{\alpha=1}^{N} g_i(q_\alpha) w_\alpha(q) g_j(q_\alpha) = \delta_{ij}, \qquad (1.2.6a)$$

$$\sum_{k=1}^{N} g_k(q_\alpha) (w_\alpha w_\beta)^{1/2} g_k(q_\beta) = \delta_{\alpha\beta}. \qquad (1.2.6b)$$

A special case of orthogonal representation is the Fourier method.[23] In this representation the orthogonal functions $g_k(q)$ are chosen as

$$g_k(q) = 1/\sqrt{L} \exp(i2\Pi kq/L), \qquad (1.2.7a)$$

where

$$k = -(N/2 - 1), \ldots 0 \ldots N/2, \qquad (1.2.7b)$$

also the sampling points are considered to be equally spaced

$$q_i = (i-1)dq \qquad (1.2.7c)$$

and L is the length of a conveniently chosen box. The choice of g (q) in eq.(1.2.6) indicates the periodic boundary conditions. This representation in conjunction with the Fast Fourier Transform (FFT)[24] algorithm scales the numerical effort semi-linearly with the phase space volume. This is the main attraction with the Fourier method representation.

The next step to representation of the wave function is the representation of operators. The result of hamiltonian operation on the wave function is the key step for determining the time evolution. Usually the hamiltonian is considered as the sum

of potential and kinetic energy operators.

$$H = T + V. \qquad (1.2.8)$$

As the potential energy operator V is local in coordinate space, its operation is just a multiplication. But the kinetic energy operator T is not local in coordinate space. One way to perform kinetic energy operation on the function x_n is to transform it to momentum space by FFT, multiplying by T and then transform it back to coordinate space by inverse FFT. Another way is to apply Finite-Difference (FD) method.[25] By invoking FD representation to T, operation of T on x gives up to second order,

$$T_{FD}\chi_n = -\hbar^2 (\chi_{n+1} + \chi_{n-1} - 2\chi_n)/2mdq^2. \qquad (1.2.9)$$

More general expressions for infinite order FD have also been given.[26] Even if the T operator is represented in other coordinate representations like spherical coordinates, the local representation is possible for the radial part of the operator by using the Bessel transform. But changing the angular parts into local representation is very complicated.

Before time propagation one has to set the initial conditions. The choice is specific for a specific problem. For bound degrees of freedom usually an eigenstate of the unperturbed hamiltonian is set equal to the initial condition. For the translational degree of freedom gaussian wave packet form is the common choice.[26(a)]

Mowrey et al. in studying the scattering problems used a method, which they termed as Close Coupling Wave Packet (CCWP)

method.[27] In this method to describe the translation motion they use wave packet evolution by means of Chebychev expansion and rotational motion using time-independent coupled Channel methods.[28] The computational effort required for CCWP method is more than that for Coupled Channel methods but the results are accurate at least for the scattering problems.

An approach which converts time-dependent periodic hamiltonians into time-independent hamiltonians is the Floquet theorem.[29] If the hamiltonian is periodic, i.e. H(t+T) • H(t), according to Floquet theorem there exists a set of Floquet modes which are particular solutions of the Schroedinger equation with unique behaviour that the density matrices are periodic. The time evolution operator U(t+T) is unitary and so in the determination of its eigenstates no spurious effects are encountered. Floquet method have been generalized to apply for the nonperiodic hamiltonians also when the system is considered in the polychromatic fields.[30]

One generalization of the Floquet method is the Quasivibrational Energy (QVE) formalism[30(a)] which give quasivibrational energies. These are useful in determining the rates of multi-photon dissociation process. Another method which provide a tool for determining the QVEs is the Complex Scaling Fourier Grid hamiltonian (CSFGH) method developed by Chu.[30(b)]

1.2.2. Dynamical Basis Set Methods:

In these methods the basis functions χ_n follow the wave packet ψ moves through space.

$$\psi(q,t) = \sum_{j=1}^{\infty} C_j(t)\, \chi_j(q,t). \qquad (1.2.10)$$

The functions x are taken to be the solutions of some reference time-dependent Schroedinger equation

$$i\dot{\chi}_n = H_0(t)\chi_n. \qquad (1.2.11)$$

Assuming that x_n remain orthogonal through out their evolution the C-coefficients are given by

$$i\dot{C}_n = \sum_m \langle \chi_n | H-H_0 | \chi_m \rangle C_n. \qquad (1.2.12)$$

The basic premise in the use of dynamical basis sets is that if H is judiciously chosen such that H-H is small then the expansion (1.2.1) requires very few terms for convergence. This feature is very advantageous when wave packet travels long distances especially for many body systems.

The important methods which provide dynamic representation are the Gaussian Wave Packet (GWP) methods, time dependent self consistent field (TDSCF) method and the Lie-algebraic methods. In the following sections we discuss these methods.

1.2.2a. Gaussian Wave packet Propagation **methods:**[31]

GWP methods are developed and extensively applied by Heller.[31,32] The main feature of GWP is that the wave function is parameterized as a complex traveling gaussian of the form

$$\psi(q,t) \approx \exp[i/\hbar\ (\alpha_t(q-q_t)^2 + p_t(q-q_t) + \gamma_t)], \qquad \textbf{(1.2.24)}$$

where q_t, p_t are the expectation values of the position and **momentum.** a is the width parameter and γ is **the** phase of the wave packet. The potential in the hamiltonian is expanded as a Taylor's series around q and **terms** beyond second order are neglected. This is known as Locally Harmonic Approximation (LHA). Substituting $\psi(q,t)$ in TDSE and comparing the coefficients **of like** powers of q-q gives the equations of motion

$$\dot{q}_t = p_t/m, \qquad \textbf{(1.2.14}$$

$$\dot{p}_t = -(\partial V/\partial q)_{q=q_t}, \qquad (1.2.15)$$

$$\dot{\alpha}_t = -2\alpha_t/m - 1/2(\partial^2 V/\partial q^2)_{q=q_t}, \qquad (1.2.16)$$

$$\dot{\gamma}_t = i\hbar\alpha_t/m + \dot{p}q_t - p_t/m - V_0. \qquad (1.2.17)$$

The eq. (1.2.14), eq.(1.2.15) are the classical Hamilton equations of motion for the system concerned and hence Heller referred this method as semiclassical GWP method. This method is exact only for harmonic potentials. It becomes an approximation for **anharmonic** potentials as the wave packet form does not remain as gaussian during propagation for these potentials. This method is also known as Thawed Gaussian Approximation (TGA).

Heller suggested an approximation over GWP which reduces the computational effort considerably. This is obtained by freezing the widths of the wave packet during the propagation and

is known as Frozen Gaussian Approximation (FGA).

Coalson and Karplus[34] and Lee and Heller[31] extended this method to obtain formally exact solution for multi-dimensional quantum mechanical problems involving anharmonic potentials. They invoke a time-dependent basis set of travelling harmonic oscillator eigenfunctions, with the width parameter controlled by local hessian as in GWP. The potential energy is expanded in Taylor's series and terms up to nth order are retained. The wave function is parameterized as

$$\psi(q,t) = f(q,t)\ \exp[g(q,t)]. \qquad (1.2.18)$$

The gaussian form is assumed for exp[(g(q,t)]. The functions f(q,t) are expanded as

$$\begin{aligned} f(q,t) &= \sum C_n(t)\ \phi_n(q,t) \\ &= \sum C_n(t)\ a_n H_n[k_t(q-q_t), \end{aligned} \qquad (1.2.19)$$

where n is the nth order Hermite Polynomial H_n and a_n and k_t are the normalization constant and width parameter. Substituting the eqs. (1.2.18) and (1.2.19) in TDSE results in the equations of motion for the parameters q_t, p_t, α_t and γ_t.

Another extension to GWP is the Generalized Gaussian Wave Packet Dynamics (GGWPD).[35] This method is an extension of GWP into complex phase space retaining time as real. This method does not restrict wave packet to be gaussian through out the propagation unlike GWP. Moreover classically forbidden regions can be explored using GGWPD. By using the symmetrized

trajectories the norm is conserved even for a superposition of gaussians. The accuracy of the results are improved over GWP.

GWP has been extensively used in determining variety of dynamics[36] such as scattering, photodissociation process, etc.. The qualitative description is good in all the applications. In the application of GWP in conjunction with time-dependent variational principle ' even quantitative accuracy was obtained for some applications.

The errors in these semiclassical GWP methods increase faster than linearly with time and so the semiclassical description may not be adequate for the systems which require the wave packet to travel longer distances. To avoid such situations Huber and Heller proposed Hybrid mechanics.[39] In this method the seniclassical description is used to construct the quantum mechanical time propagator for a finite time step, then using this propagator the evolution of the system is determined quantum mechanically for longer times.

1.2.2b. Time-Dependent Self-Consistent Field Methods:[40"60]

TDSCF method is often referred as Time-Dependent Hartree (TDH) method. The computational effort scales linearly with number of modes in the system and so even the many mode system dynamics can be attempted to study using this method. It has been suggested[40] in the early days of quantum mechanics itself but its exploration appeared much latter. The early applications[41] were to study the excitation spectra of multi-electron systems, dynamics of nuclear reactions such as fission, fragmentation and compound nucleus formation etc.. Heller[42( )] discussed TDSCF in

the context of time dependent variational principle. Harris[421] discussed first in the context of vibrational spectroscopy. Quite a number of studies on TDSCF appeared in recent years.

Each mode in the system is formally separated in **the** TDSCF method and is governed by time-dependent average potential which, is obtained by averaging the full potential over all the other modes. To this end the wave function is expanded as a single Hartree product of each mode function

$$\psi(q_1,q_2\cdots q_N,t) = \prod_{i=1}^{N} \phi_i(q_i,t), \qquad (1.2.20)$$

where N is the number of degrees of freedom in the system concerned. Writing hamiltonian for the system in simple form

$$H = \sum_i T_i + V(q_1,q_2\cdots q_N), \qquad (1.2.21)$$

with T , the kinetic energy of the ith mode and V is the potential energy. By invoking the variational principle $\langle\delta\psi|H-id/dt|\psi\rangle=0$, the SCF equations are obtained as

$$i\hbar\, d\phi_i(q_i,t)/dt = h_i^{SCF}(q_i,t)\ \phi_i(q_i,t). \qquad (1.2.22)$$

The TDSCF ith mode hamiltonian is

$$h_i^{SCF}(q_i,t) = h_i(q_i) + \bar{V}_i(q_i,t), \qquad (1.2.23)$$

where

$$h_i(q_i) = T_i + V_i(q_i) \qquad (1.2.24)$$

and

$$\bar{V}_i(q_i,t) = \sum_{i\,j} \langle\phi_j|\, V_{ij}(q_i,q_j) + \ldots \,|\phi_i\rangle. \qquad (1.2.25)$$

The single-mode description of TDSCF is represented by **eq. (1.2.23) with** each mode having its own **hamiltonian.** Here the **time evolution** of the system is governed by the time-dependent SCF potential (eq. (1.2.25)) and the evolution of the ith mode depends indirectly on the other modes through this average potential.

The TDSCF method conserves the total energy of the system, i. e.

$$d/dt \langle\psi|H|\psi\rangle = 0. \qquad (1.2.26)$$

This property is important for energy transfer studies. The **norm** of the wave function is also conserved in this formulation as the **hermiticity** of the **hamiltonian** is not affected.

From studies of nuclear dynamics it was found that TDSCF suffer from spurious state problem due to the restrictions imposed on the wave packet. Methods have proposed to eliminate this problem.[41] Average properties such as dissociation life times, single-mode energy distribution are predicted well, where as correlation between states or state to state transition probabilities are badly reproduced by TDSCF as expected.

Gerber et al.[43] developed different versions of TDSCF. In the fully quantum mechanical version of the method the functions $\phi_i(q,t)$ are expanded in terms of eigenstates $u_v(q_i)$ of the bare mode hamiltonian $h_i(q_i)$

$$\phi_i(q_i,t) = \sum C_{iv}(t)u_v(q_i)\ \exp[-i\varepsilon_v^i(t)], \qquad (1.2.27)$$

where energies ε_v^i are eigenvalues of h (q) and C $_v$ are unknown coefficients. Substitution of eq.(1.2.27) in the TDSE results in the standard set of coupled first order differential equations for C . The TDSCF potentials then appear in the form

$$\bar{V}_i(q_i,t) = \sum_j \sum_{v,w} c^*_{jv}c_{iw} \langle u_v^j|V_{ij}(q_i,q_j)|u_w^i\rangle \times \exp[-it(\varepsilon_v^j - \varepsilon_w^i)/\hbar]. \qquad (1.2.28)$$

Buch et al.[44] have explored the utility of the classical limit of TDSCF. In the self-consistent trajectory bundles approach the average potential may be written in terms of trajectories:

$$\bar{V}_i^{SCF}(q_i,t) = 1/N_t \sum_h \sum_{\lambda=1}^{N_t} V(q_i,q_h^{(\lambda)}(t)). \qquad (1.2.29)$$

The $q^{(\lambda)}$ (t) trajectory is calculated from TDSCF nth mode hamiltonian labelled by A and N_t is the number of trajectories employed. The trajectory equations for the q (t) in correspondence with single-mode TDSCF Schroedinger equation (eq.1.2.22) appear as

$$\dot{q}_i(t) = (\partial h_i^{SCF}/\partial p_i), \qquad (1.2.30)$$

$$\dot{p}_i(t) = -[\partial h_i^{SCF}/\partial q_i(t)]. \qquad (1.2.31)$$

Here h^{SCF} is classical analog of eq.(1.2.23). In this scheme $N.N_t$ equations are needed to solve the system.

Application of TDSCF in the classical limit to dissociation dynamics of several van der Waals complexes by Buch et al.** showed that it works well for both weak and strong coupling dissociation dynamics in semi-quantitative way in accordance with the experimental and quantum mechanical results.

The convergence of the results of TDSCF method depends on the choice of the coordinates. This generally done by physical intuition or by looking for the natural separability of the modes. It is proved that the optimized coordinates produce better results. The main draw back of the TDSCF is that important correlations between various modes are left out, which describe many important chemical processes. Hence TDSCF fails in determining the long time dynamics, i.e. when the correlations become significant. Attempts have made to correct for these correlations at the same time retaining the simplicity of the mean-field description.

The Time-Dependent Rotated Hartree (TDRH) method developed by Cederbaum et al.[54,55] is one of the extended versions of TDSCF method. In this method inclusion of time-dependent unitary operators acting on the Hartree product made possible the description of correlations between various degrees of freedom to a limited form. In this approximation the exact wave function is written as

$$\psi_j(t) = \prod_{k=1}^{N} U_k \phi_j(t), \qquad (1.2.32)$$

where

$$U_k = \exp(i\alpha_k A_k). \qquad (1.2.33)$$

U_k is considered as unitary and so α are real parameters and A_k are **hermitian** operators. The operator U is chosen such that it involve all possible operators which cause the mixing of different degrees of freedom. This made possible the inclusion of correlations to certain extent. The ansatz (1.2.32) is **termed** as **TDRH** wave function as U_k describe the generalized rotations.

By employing Lagrange variational principle on TDSE, the equation to be solved is[37]

$$\mathrm{Re} \langle \delta\psi | i\partial/\partial t - H | \psi \rangle = 0, \qquad (1.2.34)$$

or by employing McLachlan variation principle[37]

$$\mathrm{Im} \langle \delta\psi | i\partial/\partial t - H | \psi \rangle = 0. \qquad (1.2.35)$$

Substitution of eq.(1.2.32) and eq.(1.2.33) in these equations yield the equations for ϕ and α_k. The SCF equations for ϕ obtained by both the variational principles are the same but for the parameters they are different.

The application of the approach to a model coupled **oscillators**[54,55] showed better converged results than TDSCF method. The computational effort involved in **TDRH** is slightly more than that involved in TDSCF method but when compared to basis set calculation it is very low.

To account for the important correlations one can add configurations to TDSCF as suggested by **Makri** and Miller[56] which

is termed as Multi-Configuration Time-Dependent Self-consistent field (MCTDSCF) method. This description allow more flexibility in the wave function which makes it possible to incorporate of the important correlations. Latter on Meyer et al.[57] derived relatively simple equations for n degree of freedom system with m configurations. They write the approximate time-dependent multi-configuration trial wave function in the form

$$\psi(q_1,q_2,\ldots q_N) = \sum_{j_1=1}^{m_1} a_{j_1}(t)\ \phi_{j_1}^{(1)}(q_1,t),\ldots \sum_{j_n=1}^{m_n} a_{j_n}(t)\ \phi_{j_n}^{(n)}(q_n,t), \tag{1.2.36}$$

where m are the number of single particle functions which build up the respective modes, n is the number of modes in the system. To eliminate the redundant configurations the condition $m_s \prod_{1=1}^{n} D_1$ is imposed. The single particle functions are assumed to be orthogonal at any time:

$$\langle \phi_i^{(k)} | \phi_j^{(k)} \rangle = \delta_{ij}. \tag{1.2.37}$$

The appearance of redundant configurations also require the condition

$$\langle \phi_i^{(k)} | \dot{\phi}_j^{(k)} \rangle = 0. \tag{1.2.38}$$

Defining the matrices $A^{(k)}$ and $\phi^{(k)}$ to make the equations look simpler

$$A_{J_n}^{(k)} = a_{j_1,\ldots j_{k-1},j,j_{k+1},j_n}, \tag{1.2.39}$$

$$\phi_j^{(k)} = \phi_{j_1}^{(1)} \ldots \phi_{j_{k-1}}^{(k-1)} \phi_{k+1}^{(k+1)} \ldots \phi_{j_n}^{(n)}, \qquad (1.2.40)$$

invoking the Dirac-Frenkel variation principle and the conditions eq. (1.2.37) and eq. (1.2.38) the working equations look as

$$i \dot{a}_{j_1 \ldots j_n} = \langle \phi_{j_1}^{(1)} \ldots \phi_{j_n}^{(n)} | H | \psi \rangle, \qquad (1.2.41)$$

$$i\dot{\phi} = \sum (A^{(k)+} A^{(k)})^{-1} A^{(k)+} [\langle \phi_j^{(k)} | H | \dot{\psi} \rangle - i \sum_l A_{jl}^{(k)} \phi_l^{(k)}. \qquad (1.2.42)$$

The application of MCTDSCF to a model coupled oscillators by Meyer et al. and other applications[57,58] showed good convergence.

Another version to MCTDSCF is TDHG-CI.[59] The strategies in the two theories are similar but they differ in detail. In MCTDSCF each basis function in each coordinate for every mode is individually optimized self-consistently with the evolution of superposition coefficients. In TDHG-CI, using McLachlan Variation, a global effective potential is constructed to guide all the travelling basis functions. Once the basis set is constructed, the configuration interaction phase is carried out in the complete basis. Application of this strategy to collinear inelastic atom-Morse oscillator scattering[59] showed that it works well for obtaining the dynamics of many body quantum systems.

In a very recent article Vekhtar et al.[60] suggested TDSCF2-CI approach which has the advantages of Pair correlations and of configuration interaction. They write ψ as

$$\psi_{\alpha\beta}(\text{TDSCF2}) = \psi_{\alpha\beta}(\alpha,\beta,t) \prod_{i\ \alpha,\beta} \psi_i(i,t), \qquad (1.2.43)$$

where (α,β) is a mode pair whose interaction has to be exactly treated. The equations for other modes are the same as in the TDSCF method. But the potential for these methods looks as

$$V_{eff}^{\alpha\beta} = V(\alpha,\beta,t) + \sum_{i\ \alpha,\beta} V_{\alpha\beta}(i,t). \qquad (1.2.44)$$

The correlated pair is chosen differently in each of the N(N-l)/2 configurations.

1.2.2c. The Lie-Algebraic construction of dynamical basis:[61]

Micha and co workers have applied the Lie algebraic method to study the atom - diatom and diatom - diatom collisions. They expand the interaction potential in Taylor series and truncate at quadratic level so that the finite dimensional quadratic Lie algebra can be used to construct a reference evolution operator to propagate the dynamical basis functions. The elements q^2, qp+pq, p^2, q, p in this order are contained in the Lie algebraic structure. The interaction picture hamiltonian is then written in terms of the elements of the algebra, X which are closed under commutation:

$$H_I(t) = \sum_k f_k(t)\ X_k. \qquad (1.2.54)$$

The reference evolution operator is then constructed as

$$U_I(t,t_0) = \prod_{n=1}^{5} \exp[-i\alpha_n(t)X_n]. \qquad (1.2.55)$$

Substituting U and H in TDSE and using Hausdorf expansion results in the governing equations for $a_n(t)$. In the case of diatom-diatom collisions, part of the interaction potential is not closed under commutation and so the algebra becomes slightly complicated. To solve this residual coupling they use the perturbation theory.

Benjamin[62] formulated a semiclassical algebraic theory in which the vibrational motion is described quantum mechanically using an appropriate algebra and the translational motion is described by classical equations of motion. For the Lie-algebraic structure when the full quadratic algebra is used he termed the method as Quadratically Driven Parametric Oscillator (QDPO) method. In a different approximation the quadratic terms are neglected and the method is termed the Linearly Driven Parametric Oscillator (LDPO) method. In another approximation a canonical transformation is performed such that it eliminates the effect of quadratic elements and the approach is termed as Qudratically Driven Scaled oscillator (QDSO). Application was made to atom - diatom and diatom - diatom collisions and the values are in good agreement with exact quantum mechanical results and the computational effort is comparatively low.

The role of time varying frequency in the vibrational transition of a nonlinearly driven oscillator is studied by Shin[63] using Lie algebraic method. The Lie algebraic structure contains the set $\{ a^+a,\ a^+,\ a,\ a \}$. The transition probabilities are computed over wide range of collision energies to study the effect of time-dependent frequency.

Gilmore and Yuan[64] have studied vibrational

translational interaction and computed the scattering matrix elements using this approach. They use group theoretic root space diagram to construct the evolution operator, the double photon algebra which is the sub algebra of C representation was used. The evolution operator in terms of a and a is then looks as

$$U(t) = \exp(ra^{+} + Ra^{+^2}) \exp(\eta\ (n+1/2)+\delta I)\ \exp(la + la^2), \quad (1.2.56)$$

where r, R, η, δ, 1, L are time-dependent functions. The convergence of the transition probabilities encouraged the extension of the method to complicated systems.

Shi and Rabitz studied a parametric amplifier and collinear collision of an atom with a Morse oscillator using a variational Lie algebraic formalism. In the study of parametric amplifier the algebraic set $\{a_1^+a_1,\ a_2^+a_2, a_1a_2, a_1^+a_2^+,\ a_1^+,\ a_1,\ a_2^+,\ a_2\}$ was used to construct the evolution operator. In the relatively complicated system of collinear collision of an atom with Morse oscillator only the relative motion was treated semiclassically using the Lie-algebraic method. The Morse oscillator part of the hamiltonian was solved by basis set expansion in Morse basis.

Kucar and Meyer solve TDSE using the dynamical basis set. In determining the time dependence of the basis set they utilize the Lie-algebraic structure to construct the evolution operator. The time-dependent basis $\{\chi\ (q,t)\}$ is defined as

$$\chi_n(q,t) = U(t)\ \phi_n(x)$$

$$= \prod_{k=1}^{m} \exp[i\alpha_k(t)A_k], \quad (1.2.57)$$

where α_k represents a real parameter and the generator A_k is a hermitian operator. The wave function $\psi(q, t)$ is then expanded in this basis as

$$\begin{aligned} \psi(q,t) &= \sum_n a_n(t)\, \kappa_n(q,t), \\ &= U(t)\, \phi(q,t). \end{aligned} \tag{1.2.58}$$

Keeping in view that the generators A_k form a Lie algebra, the evolution operator is constructed as

$$\begin{aligned} U(t) = {} & \exp(-iq_t p)\, \exp(ip_t q)\, \exp(ib_t q^2) \\ & \times \exp(ia_t(qp+pq)\, \exp(i\gamma_t H_0)\, \exp(i\delta_t), \end{aligned} \tag{1.2.59}$$

where the operator set $\{1, q, p, q^2, (qp+pq), H\}$ forms a Lie algebra. The working equations are derived for a multi-dimensional system. The system is well represented in the time-dependent basis but the problem is that the differential equations to be solved may become stiff in the course of the time propagation.

Echave et al.[67] have applied the Lie-algebraic theory to build the interaction potential in the intermediate picture and used it to calculate the physical observables. They write the TDSE in terms of H_{eff} and U_{eff} as

$$i\hbar\, dU_{eff}(t,t_0)/dt = H_{eff} U_{eff}(t,t_0), \tag{1.2.60}$$

where

$$U_{eff}(t_0,t_0) = 1.0. \tag{1.2.61}$$

The wave function is then represented as

$$\psi(t) = U_{eff}(t,t_0)\ \phi(t). \qquad (1.2.62)$$

They write the equation for the ϕ (t) as

$$ih\ d\phi(t)/dt = H_I\ \phi(t), \qquad (1.2.63a)$$

$$\phi(t_0) = \psi(t_0), \qquad (1.2.63b)$$

where H is defined in terms of H and U

$$H_I = U_{eff}\ (H - H_{eff})\ U_{eff}. \qquad (1.2.64)$$

H is expanded as

$$H_{eff} = \sum_{i=1}^{n} h_i x_i, \qquad (1.2.65)$$

where {x_1, x_2, ... x_n) is a set of hermitian operators. The formation of H matrix is facilitated by defining

$$x_j'(t) = \sum_{k=1}^{n} G_{jk}(t)\ x_k. \qquad (1.2.66)$$

The time-dependent matrix elements G satisfy linear equations of motion. Another matrix F is defined such that

$$[x_j, H_{eff}] = \sum_{k=1}^{n} F_{jk} x_k. \qquad (1.2.67)$$

The matrix G satisfy the equation

$$ih\, dG/dt = FG, \quad G(t_0) = 1.0. \tag{1.2.68}$$

The working equations are eq.(1.2.63), (1.2.64) and eq.(1.2.68). An application was made to study the VT transfer in He - H_2 collisions.

An application of algebraic theory to determine the photodissociation dynamics of CH I was made by Someda et al.[68] They define the evolution operator as

$$U(t) = \prod_{i=1}^{m} \exp\,[i\eta_i(t)\, X_i], \tag{1.2.69}$$

where (X_1, X_2, ...X_m) form a Lie algebra. The coefficients η are determined by employing Dirac- Frenckel time-dependent variational principle.

Recently Lin et al.[69] analyzed the molecule-surface collisions of ^4He and ^3He on the (001) face of LiF crystal using Lie-algebraic method. They have used the six dimensional algebra which contains the elements I, a, a, aa, a , a to construct the evolution operator.

1.2.3 Integration Schemes:

The propagation of wave function in time requires the construction of evolution operator. The formal solution to U in eq.(1.0.4) is

$$U = \exp(-iHt/\hbar). \tag{1.2.70}$$

The construction of evolution operator in this way is generally impossible as the exponentiation of the hamiltonian is a complicated job. To simplify the construction of evolution operator one can expand the above expression in Taylor's series and truncate the expansion after few terms. The simplest is to write

$$U = 1 - iHdt/\hbar. \qquad (1.2.71)$$

This approximation to the evolution operator in conjunction with finite difference formula for the second derivative of the coordinate in the kinetic energy operator provide an explicit integration scheme. This scheme is known as the crude Euler method. This explicit scheme is known to be unstable as it does not conserve the time reversal symmetry of the Schroedinger equation.

McCullough and Wyatt used Crank-Nicholson approximation to the evolution operator. In this approach U is approximated as

$$U = [\, 1 + iHdt/2\hbar \,]^{-1} [\, 1 - iHdt/2\hbar \,]. \qquad (1.2.72)$$

This approximation provides an implicit integration scheme along with finite difference formula for kinetic energy operator. In implicit integration scheme a system of equations need to be solved. While stable it requires high computational effort because it involves inversion of matrices.

A stable integration scheme was developed by Askar and

Cakmak[71] in which they use the symmetric relation

$$\psi(t+dt) - \psi(t-dt) = [\exp(-iHdt/\hbar) - \exp(iHdt/\hbar)]\, tfi(t). \quad (1.2.73)$$

Expanding the above two exponential terms in Taylor's series and truncating it after two terms results in the explicit second order differencing propagation scheme

$$\psi(t+dt) = \psi(t-dt) - (2iHdt/\hbar)\, \psi(t). \quad (1.2.74)$$

This scheme preserves norm and energy if the hamiltonian operator is hermitian. This energy and norm conservation accumulates error in the phase. This becomes significant after certain steps of time propagation.[5] This is the propagation scheme used in many applications of the finite difference and Fourier methods.[72] Formulae for higher order schemes were discussed by Manthe and Koppel.[73]

Fiet and Fleck developed a split time propagation scheme.[7*] In this the evolution operator in eq. (1.2.70) is split into two operators in which one consists of potential energy operator and the other kinetic energy operator. These two operators propagate the wave function separately.

$$\exp(-iHdt/\hbar) \approx \exp(-iTdt/2\hbar)\, \exp(-iVdt/\hbar)\, x \exp(-iTdt/2\hbar). \quad (1.2.75)$$

This method is used generally in conjunction with FFT. In this method norm is conserved as each split time evolution operator is

unitary, but error accumulates due to non commutability of kinetic and potential energy operators.

In these short time propagation schemes error accumulation is inevitable somewhere in the time propagation. For the time-independent hamiltonians one can define a global propagator in which a polynomial expansion is used for the evolution operator.

$$U(t) \approx \sum_{n=0}^{N} a_n \phi_n (-iHt/\hbar). \qquad (1.2.76)$$

Here ϕ are elements of some orthogonal polynomial set. Chebychev and Lanczos schemes have been shown to provide good expansions for these global propagator schemes. In the Chebychev scheme[23*1] ϕ_n are the complex Chebychev polynomials. The determination of propagated wave function in this scheme requires the operation $\phi_n(-iH)$, which can be calculated using the Chebychev recursion formula,

$$\phi_{n+1} = -2iH\,\phi_n + \phi_{n-1}.$$

The error accumulation is minimal in this scheme and it is uniformly distributed on all the eigenvalues and so the Chebychev polynomial expansion is optimal for the global propagators.

In the Lanczos scheme[75] the recurrence relation for $\phi_n(-iH)$ is

$$\beta_j \phi_{j+1} = [H - \alpha_j]\,\phi_j - \beta_{j-1}\,\phi_{j-1}, \qquad (1.2.78)$$

where

$$\alpha_j = \langle \phi_j | H | \phi_j \rangle . \qquad (1.2.79)$$

(3 is obtained from the normalization condition

$$\langle \phi_{j+1} | \phi_{j+1} \rangle = 1. \qquad (1.2.80)$$

The error accumulation is not uniform in this scheme and hence requires the stabilization procedures.[5]

These two schemes are independent of the representation of the wave function. In these global evolution methods no intermediate results are obtained. One can split the propagation into smaller intervals in order to get the intermediate values but large increase in the number of intervals make the approach inefficient. In many applications, Chebychev ' and Lanczos recurrence schemes have been used for time propagation.

To deal with N-level systems a simple computational technique called as time-slicer has been suggested by Hirschfelder et al.[37] In this procedure the time-dependent hamiltonian is approximated by a sequence of time-independent hamiltonians. At nth period H(t) is approximated by a constant hamiltonian (for a very small time period) $H^{(n)}$, which can be written as

$$H^{(n)} = H[(t_n + t_{n-1})/2]. \qquad (1.2.81)$$

Since this technique does not require hamiltonian to be hermitian the effects of natural lifetimes and the other relaxation parameters which we generally encounter in Electron Spin Resonance (ESR) and Nuclear Magnetic Resonance (NMR) applications can be

determined. The time-slicer method is a simple and efficient numerical procedure for the solution of both linear and nonlinear sets of coupled first and second order differential equations.

1.3. NON-PERTUBATIVE APPROACHES

In this section we discuss three non-pertubative and non-variational methods: the construction of the evolution operator by Lie-algebraic methods, the time-dependent coupled cluster method (TDCCM) and by the path integral approach.

1.3.1. Lie-algebraic construction of U:[80]

As noted earlier, the Lie-algebraic methods have been mostly used to define dynamical basis set representation. However they can be used to construct the exact time evolution operator also. The algebraic approaches are developed on the realization that when the hamiltonian is an element of a Lie algebra, then the time evolution operator can be written as an exponential of a general linear combination of the elements of the algebra. The hamiltonian is expressible as

$$H = \sum_n h_n A_n, \qquad (1.3.1)$$

where all the operators A_k belong to the set L that is closed under commutation

$$[A_n, A_m] = \sum_k C_{nm}^k A_k ; \; A_n, A_m, A_k \in L, \; \forall \; n, m, k \qquad (1.3.2)$$

The time evolution operator can then be written as an exponential of a general linear combination of all the operators of the **algebra,**[9] i.e.

$$U(t) = \exp\left[\sum_n a_n A_n\right], \qquad (1.3.3)$$

alternatively in the Wei-Norman product form as

$$U(t) = \prod_n \exp\left[a_n A_n\right]. \qquad (1.3.4)$$

The variables a are time-dependent coefficients of the generators of the evolution operator. The governing equations for these coefficients are obtained by appealing to the TDSE **(eq.(1.0.4)).** One can chose perturbative Magnus expansion[8] method or any nonperturbative approach[80] to construct the evolution operator.

The algebraic approach is practical particularly when the concerned Lie algebra is finite dimensional. In that case the number of variables required to define the evolution operator are finite even if the system is considered in an infinite dimensional Hilbert space. Harmonic oscillator algebra is a finite dimensional algebra and is commonly used in the construction of the evolution operator for the quadratic **hamiltonians** which are elements of this algebra. Projection operator algebra is another algebra which is finite dimensional. The solution for **the** coefficients a_n is not trivial if the algebra is not **semisimple.**

A subset S of a Lie algebra L is called a subalgebra if it is closed under commutation, addition and multiplication by a scalar. A subalgebra S is called an ideal if all the commutators [X, Y] of

X ∈ S and Y ∈ L is in S. The union of all the solvable ideals is called the radical, where the union of two ideals is again a solvable ideal. An algebra is said to be semisimple if its radical is {0}. An algebra is said to be simple if it has no ideal other than L and {0}, and if the derived algebra (the set of the elements of L which are the result of the commutation of the two Lie elements) L not equal to (0).

If the evolution operator is considered in the Wei-Norman product form[80] as in eq.(1.3.4) the global solutions are possible in a number of cases, for example when the Lie algebra to which the hamiltonian belongs is a solvable algebra. It has also been proved that if the Lie algebra from which the evolution operator is constructed is not a simple algebra then the equations of motion for the different sets of coefficients are decoupled.[80,81]

Wolf and Korsch[81] developed a theory utilizing the Levi-Malcev decomposition of finite dimensional Lie algebras and the Wei-Norman representation to the evolution operator for the application of time-dependent quantum systems. Levi-Malcev theorem states that every finite dimensional algebra L is the semidirect sum of its unique radical (i.e. the maximal solvable ideal), R and semisimple algebra S isomorphic to the factor algebra L/R. From this theorem the eq. (1.0.4) can be decomposed as

$$idU_S/dt = H_S U_S, \tag{1.3.5}$$

and

$$idU_R/dt = (U_S^{-1} H_R U_S)\, U_R, \tag{1.3.6}$$

where

$$H = H_S + H_R \ , \ H_S \in S \text{ and } H_R \in R. \qquad (1.3.7)$$

U is then written in a product form

$$U = U_S \, U_R. \qquad (1.3.8)$$

From the theorem which states **that every finite dimensional semisimple** Lie algebra S can **be uniquely decomposed** into **a** direct **sum** of simple ideals

$$S = S_1 \oplus \ldots \oplus S_k, \qquad (1.3.9)$$

it is found that the effort in finding U can be reduced by writing U as

$$U_S = U_1 \, U_2 \ldots U_k, \qquad (1.3.10)$$

with

$$idU_1/dt = H_1 U_1, \qquad (1.3.11a)$$

$$idU_2/dt = H_2 U_2, \qquad (1.3.11b)$$

$$\ldots\ldots$$

$$idU_k/dt = H_k U_k. \qquad (1.3.11c)$$

In this way the problem is reduced to solving the smaller subordinate problems and U is factored and written in the Wei-**Norman** product form. The advantage in writing this form is that for solvable algebras, there exists an ordering of the basis **for** which the product form gives the global solution.[80]

Alhassid and **Levine**[82] developed a Lie-algebraic approach

to solve the dynamics in any general system. In their formalism for a specific application of linearly displaced harmonic oscillator the evolution operator is constructed as the exponential of the linear combination of the elements of six dimensional quadratic Lie algebra.

1.3.2 The time-dependent coupled cluster method:[83]

The time dependent coupled cluster method is a time dependent generalization of coupled cluster theory of Coetser and Kuemmel.[83] The feature of CCM is that the evolution operator U is written as an exponential of the cluster operator S.

$$U = \exp(S), \tag{1.3.12}$$

$$S = S_1 + S_2 + \ldots, \tag{1.3.13}$$

and the wave function is given by

$$\psi = \exp(S) \, |0\rangle. \tag{1.3.14}$$

The cluster operator is then expanded in terms of one, two,... body excitation operators. The equations for S are obtained by projecting on to the Schroedinger equation. In the TDCCM the cluster operators S are chosen to be time-dependent

$$S = \sum_{i=1}^{\infty} S^{(1)}(t). \tag{1.3.15}$$

The TDCCM equations are obtained from projecting the wave function

on to the TDSE and left multiplying with exp(-S)

$$i\hbar \exp(-S)\ (d/dt)\ \exp(S) = \exp(-S)\ H\ \exp(S). \qquad (1.3.16)$$

The expression exp(-S) (d/dt)exp(S) is usually determined by using Hausdorf expansion,

$$\exp(-S)\ (d/dt)\ \exp(S) = d/dt + S + 1/2!\ [S, S] + \ldots \qquad (1.3.17)$$

This time-dependent generalization to CCM is first suggested by Hoodbhoy and Negele[84] and by Schoenhammer and Gunnersson[85]. Hoodbhoy and Negele employed TDCCM for determining the nuclear dynamics. Specifically truncations appropriate to strongly repulsive cores were discussed. The system they considered consists of n-particle and n-hole states. The wave function is written as

$$|\psi> = \exp(\sum_m S_m). \qquad (1.3.18)$$

Using eq. (1.3.16) the following equations emerge

$$<\phi|\ (H - i\partial/\partial t\ |\psi> = 0, \qquad (1.3.19a)$$

$$<\phi|\ a_p^+ a_h\ (H - i\partial/\partial t)|\psi> = 0, \qquad (1.3.19b)$$

$$<\phi|\ a_{p_1}^+ a_{p_2}^+ a_{h_1} a_{h_2} (H - i\partial/\partial t)|\psi> = 0, \qquad (1.3.19c)$$

$$\langle\phi|\, a^{+}_{p_1}\ldots a^{+}_{p_n}\, a_{h_1}\ldots a_{h_n}\,(H - i\partial/\partial t)\,|\psi\rangle \;=\; 0, \qquad \textbf{(1.3.19d)}$$

where p and h are occupied and unoccupied states. Writing $S^n(t)$ in arbitrary time-dependent basis

$$S^n(t) = \sum_{p_1,h_1} \langle p_1\ldots p_n|S^n(t)|h_1\ldots h_n\rangle a^{+}_{p_1}\ldots a^{+}_{p_n} a_{h_1}\ldots a_{h_n} \qquad (1.3.20)$$

and

$$d/dt\; a^{+}_{\alpha} \;=\; \sum \langle\beta|\dot{\alpha}\rangle\; a^{+}_{\beta}. \qquad \textbf{(1.3.21)}$$

The time derivative terms of eq.(1.3.19) becomes

$$\langle\phi|\, a^{+}_{p_1}\ldots a^{+}_{p_n}\, a_{h_1}\ldots a_{h_n}\; i\partial/\partial t)\,|\psi\rangle \;=\; i\partial/\partial t\;\langle h_1\ldots h_n|\psi_n|p_1\ldots p_n\rangle$$

$$-i\langle\dot{p}|\alpha\rangle\langle\phi|a^{+}_{p_1}\ldots a^{+}_{p_n}\, a_{\alpha}\, a_{h_1}\ldots a_{h_n}\,|\psi\rangle. \qquad \textbf{(1.3.22)}$$

Schoenhammer and Gunnerson[85] applied TDCCM to obtain the core - level spectra of adsorbed atoms and molecules taking the coulomb repulsion in the adsorbate valence level into account. They define $|\phi(t)\rangle$ as

$$|\phi(t)\rangle \;=\; N(t)\; \exp(S(t)|\phi_0\rangle, \qquad \textbf{(1.3.23)}$$

where N(t) is the normalization factor. The working equations are obtained by using eq.(1.3.15), eq. (1.3.16) and eq. (1.3.17):

$$i\,\dot{N}(t) \;=\; \langle\phi_0|H(t)|\phi_0\rangle N(t), \qquad \textbf{(1.3.24a)}$$

$$i\dot{S}^{(n)}_{\alpha_1,\ldots\alpha_n,\mu_1,\ldots\mu_n} = \langle\alpha_1\ldots\alpha_n,\mu_1\ldots m_n|\bar{H}(t)|\phi_o\rangle, \qquad (1.3.24b)$$

where

$$|\alpha_1\ldots\alpha_n,\mu_1\ldots\mu_n\rangle = a^+_{\alpha_1}\ldots a^+_{\alpha_n}a_{\alpha_1}\ldots a_{\alpha_n}|\phi_o\rangle. \qquad (1.3.24c)$$

Eqs. (1.3.24) are n coupled nonlinear differential equations. When H contains m-body interactions, the n number of equations can be truncated after m. For the system of noninteracting electrons the equation reduces to single nonlinear differential equation and it is the exact solution for the problem.

Arponen introduced a biexponential form to the evolution operator in the coupled cluster framework. Expectation values are easily obtained in this formalism. The usual exp(S) is written as exp(S)exp(S), where S and S are the excitation and deexcitation operators respectively. $|\psi\rangle$ and $\langle\psi|$ are then defined by

$$|\psi\rangle = \exp(S)\,|\phi\rangle, \qquad (1.3.25a)$$

$$\langle\psi'| = \langle\phi|\exp(S') \qquad (1.3.25b)$$

and

$$S = \sum_{h,p} s_{ph}a^+_p a_h, \qquad (1.3.25c)$$

$$S' = \sum_{h,p} s'_{ph}a^+_p a_h, \qquad (1.3.25d)$$

where a^+ and a are the creation and annihilation operators and s and s' are the numerical amplitudes. The time dependence of the cluster operators S and S are established by using

time-dependent variational principle. A functional A is constructed such that

$$A\,[\psi,\ \psi'] \;=\; \int dt\ \langle\psi'(t)|[i\partial/\partial t - H(t)|\psi(t)\rangle. \qquad (1.3.26)$$

The TDSE equations for the bra and ket states are obtained by **requiring A to** be stationary with respect to arbitrary variations of ψ (t) and ψ (t) respectively. In the exp(S) form of writing

$$A[S,\ S'] \;=\; \int dt\ \langle\phi|\exp(S'(t))\exp(-S(t))[i\partial/\partial t - H(t)]|\psi(t)\rangle. \qquad \textbf{(1.3.27)}$$

The normalization is performed by requiring $\langle\psi'|\psi\rangle = 1$. Thus

$$\begin{aligned} A &= i\int dt\ \langle\phi\ |\exp(S')\dot{S}|\phi\rangle - i\int dt\ T_H(t), \\ &= -i\int dt\langle\phi|\exp(S')S''S|\phi\rangle - i\int dt T_H(t), \end{aligned} \qquad (1.3.28a)$$

$$T_H\,[S,\ S''] \;=\; \langle\phi|\ \exp(S')\exp(-S)\ H\ \exp(S)|\phi\rangle. \qquad (1.3.28b)$$

The partial integration of eq. (1.3.28a) yields the equations of motion for the cluster amplitudes S and S :

$$i\sum_j k_{ij}\dot{S}_j \;=\; \partial T_H/\partial S_i'', \qquad \textbf{(1.3.29a)}$$

$$i\sum \dot{S}_j' k_{ji} \;=\; -\partial T_H/\partial S_i. \qquad (1.3.29b)$$

Here

$$k_{ij}[S''] = \langle\phi \mid C_i \exp(S'')C_j^+ \mid \phi\rangle. \qquad (1.3.29c)$$

This approach is restricted to systems represented by single -reference function at t=0. Extension to multi-reference systems is not trivial.

The TDCCM has been employed by Sebastian[87] to study the ion neutralization scattering. In this system the ion is such that it has a closed shell structure with one empty orbital outside the shell, which can take up at the most two electrons from the metal surface. The S operator is defined as a linear combination of all possible single particle - hole excitation operators and S as a linear combination of all two particle-hole excitation operators, which transfer two electrons to the orbital of the ion from the solid. The cluster operators S for n > 2 are neglected. For treating an ion which leaves the surface the TDCCM is a better alternative where the time-dependant Hartree Fock (TDHF) fails.

[88]

Durga Prasad has developed TDCCM theory to calculate molecular absorption spectra of systems on multi dimensional anharmonic surfaces. The calculation involves the evolution of the door way state $|\phi>$ under the influence of the vibrational hamiltonian of the upper surface H . The molecular hamiltonian is represented as

$$H(\alpha) = E_\alpha + \sum_I w_I(\alpha) a_I^+ a_I + \sum_I V_I(\alpha)\ (a_I^+ + a_I) + 1/2! \sum_{IJ} V_{IJ}(\alpha)\ (a_I^+ + a_I)\ (a_J^+ + a_J) + \ldots, \qquad (1.3.30)$$

where α is the index of the electronic state, E_α is the vertical

excitation energy. w are the frequencies and V etc. are the various anharmonicity constants. a and a are the creation and annihilation operators of the Ith mode. The doorway state is approximated by

$$|\phi_q\rangle = |0\rangle \qquad (1.3.31a)$$

because the anharmonicities rarely effect the vibration less state, where $|0\rangle$ is the vacuum state for the operator a .

$$a_I |0\rangle = 0. \qquad (1.3.31b)$$

The Wei - Norman product form is assumed for the evolution operator. Writing it in the normal order form and eliminating the operators which give zero acting on $|0\rangle$, the evolution operator is given by

$$U(t) = \exp[S_0 + \sum s_I a_I^+ + \sum s_{IJ}^2 a_I^+ a_J^+ + \ldots], \qquad (1.3.32)$$

where

$$S_1 = \sum s_I^1 a_I^+, \qquad (1.3.33a)$$

$$S_2 = 1/2! \sum_{IJ} s_{IJ}^2 a_I^+ a_J^+, \qquad (1.3.33b)$$

and etc. The S is a complex scalar.

The time evolution of the state $|0\rangle$ is given by

$$|t\rangle = \exp(-iH_e t)|0\rangle = \exp(S)|0\rangle. \qquad (1.3.34)$$

The equations for the cluster amplitudes s_i etc. are obtained by

appealing to TDSE and by projecting on to the different excited states.

$$i\dot{S}_m = \langle m|\bar{H}_e|0\rangle, \tag{1.3.35a}$$

where

$$\bar{H}_e = \exp(-S)\, H_e \exp(S). \tag{1.3.35b}$$

These are a set of coupled nonlinear differential equations to be integrated by subjecting to the initial conditions

$$S_m(0) = 0. \tag{1.3.35c}$$

The Fourier transform of $\exp(S_0)$ gives the molecular absorption spectra.

Very recently Sastry et al.[89] developed a Lie algebraic approach for the construction of evolution operator on anharmonic potential energy surfaces without invoking any basis sets at any stage of its construction. They have constructed the evolution operator using boson ladder operators. Application to atom-diatom collisions proved the validity of the theory. Sastry et al.[90] have also studied the photodissociation process using TDCCM in the boson representation formalism.

A multi-reference TDCCM has been employed by Guha and Mukherjee.[91] They generalize the effective hamiltonian theory to encompass the nonstationary situation in the TDCCM formalism. A set of nonstationary states at some initial time t_0 are defined by

$$\psi_k^0(t_0) = \sum_i C_{ik}(t)\phi_i, \tag{1.3.36}$$

where ϕ are a set of quasi degenerate strongly interacting

functions spanning the model space. ψ_k^0 evolve in time according to

$$\psi_k(t) = U(t,t_0)\ \psi_k^0(t_0)$$

with U satisfying eq.(1.0.4). The evolution operator U is factorized as

$$UP = U_{ex}U_M P, \tag{1.3.38}$$

where U_M is the model space evolution operator and U brings the admixture of complimentary space function. U_M satisfies the equation

$$\psi_k^0(t) = U_M(t,t_0)\ \psi_k^0(t_0) \tag{1.3.39}$$

and

$$i\partial U_M(t,t_0)/\partial t = H_{eff}(t)U_M(t,t_0). \tag{1.3.40}$$

Here H_{eff} is the model space time-dependent effective hamiltonian. Using the above relations the equation for U is written as

$$i\partial U_{ex}/\partial t = HU_{ex} - U_{ex}H_{eff} \tag{1.3.41}$$

with H_{eff} defined by

$$H_{eff} = [U_{ex}^{PP}]^{-1}\ [[HU_{ex}]^{PP} - i\partial U_{ex}^{PP}/\partial t. \tag{1.3.42}$$

The evolution U^{QP} is governed by

$$i\partial U_{ex}^{QP}/\partial t = [HU_{ex}]^{QP} - U_{ex}^{QP}\ H_{eff}. \tag{1.3.43}$$

U_M and U_{ex} are defined by

$$U_M = \{\exp(X)\}, \quad \textbf{(1.3.44a)}$$

$$U_{ex} = \{\exp(S)\}. \quad \textbf{(1.3.44b)}$$

Here X is a closed cluster operator written in **the normal order** and S are the external operators U_M and U_{ex} are **taken to be** normally ordered exponential ansatze (denoted by **the** braces in **eq.(1.3.54)).** The hamiltonian of the system is considered as

$$H(t) = \sum_i h_i(t) l_i,$$

where **h** (t) are time-dependent matrix elements **and 1 are suitable** creation **and** annihilation operators defined in the **Fock** space. The working equations are

$$i\partial S/\partial t = \{\overline{HU}_{ex}\} - \{\overline{U_{ex}^{\dagger} H_{eff}}\}, \quad \textbf{(1.3.46a)}$$

$$i\partial X/\partial t = \{\overline{H_{eff} U_{ex}}\}. \quad \textbf{(1.3.46b)}$$

Here the notation bar on the expression **indicates that they are** connected and curly bracket normal ordering **of the operators.** Application to 3 dimensional rotated Harmonic **oscillator was** presented.

1.3.3 Path integral based approaches:

In this class of methods the time evolution operator is

written as the product of several short time propagators.

$$\langle i|U(nt)|j\rangle = \sum \langle i|U(t)|n_1\rangle\langle n_1|U(t)|n_2\rangle\langle n_2\rangle\ldots\langle n_f|U(t)|j\rangle. \quad \textbf{(1.3.47)}$$

For certain classes of systems in which the irrelevant degrees of **freedom** can be treated as harmonic bath variables and for certain types interaction potentials the propagators in eq. (1.3.47) can be factorised and averaging over the bath variables can be carried out. Consequently the numerical effort does not scale exponentially with the number of degrees of **freedom.** On the negative side the number of paths increases exponentially with the number of intermediate states included. However, under some conditions this approach is more attractive than traditional basis set approach. Makri[92] and co workers used it extensively to study several model problems. More recently Domcke and co **workers**[93] used a similar approach to study nonadiabatic dynamics in some model systems.

1.4. SCOPE OF THE PRESENT WORK

As can be seen from the discussion above the various methods available to date, while being powerful, suffer from **some** lacuna or the other. The Dyson perturbation theory for example generates nonunitary approximation to the evolution operator **and** thus might lead to norm violation. The exponential perturbation theories such as Magnus expansion are subject to questions regarding the existence of solutions to the working equations. It

is thus desirable to develop alternative pertubation theories.

The variational methods based on linear basis set expansions are capable of providing any desired accuracy and are easy to implement. However, the expansions are slow to converge and for systems with several degrees of freedom the basis set size increases exponentially with the number of degrees of freedom in the system. In addition these approaches do not provide any intuitive picture of the physical process under study. For example it is known that the IVR is dominated by the sequence of overlapping nonlinear resonances. Energy transfer through such resonances is essentially a two body process. A straight forward linear basis set expansion does not reflect, or make use of, this information. It is thus desirable to develop approaches in which the dynamics of the system can be viewed in terms of the subsystems in a transparent manner. Development of such approaches forms the subject matter of our thesis.

The Lie-algebraic construction of the time evolution operator provides the formal framework for our discussion. We develop in Chapter II a reduction principle by which the evolution operator can be written in a non-canonical product form based on the sub-algebraic structure present in the operator space. The working equations for the coefficients of different groups of generators are decoupled in this approach even when the spectrum generating algebra is simple. This result goes beyond an earlier principle discussed by Wei and Norman and Wolf and Korsch.[81] We then use this principle to develop a form of degenerate pertubation theory. The origin of norm violating intruder states is analyzed. We then present some model studies on an

harmonically driven Morse oscillator to assess the convergence properties of this perturbation theory.

We next explore the sub-algebraic structure present in the operator set present in the Fock space in Chapter III. The evolution operator constructed in the Fock space is essentially the one obtained by the TDCCM using an ordinary exponential ansatz. It turns out that different sub-algebraic sequences lead to different versions of CCM. Some of these are explicitly shown.

The CCM is a very popular approach in the electronic structure theories.[95] It is known that the CCM provides highly accurate approximations even at a low truncations due to its exponential structure. In Chapter IV we study the dynamics of IVR in a model hydrocarbon chain to see if the similar many body structure exists that can be exploited in this class of problems. It turns out that the TDCCM with a two body cluster operator is quite accurate up to about four vibrational periods indicating the utility of TDCCM.

In the next chapter we use TDCCM to follow the dynamics of an initially prepared state in a coupled two state many mode system. The hamiltonian is taken from a linear coupling model.[96] Unlike the IVR problem studied in Chapter IV this system is not dominated by resonances. It is known from the earlier studies that TDSCF provides a good zeroth order description for this system. We formulate TDCCM in a dynamical basis generated by TDSCF. The TDCCM at two body level improves upon the TDSCF within the time period of our study. The last chapter summarizes the conclusions of our studies.

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CHAPTER II

DEVELOPMENT OF EXPONENTIAL PERTURBATION THEORIES

2.1. INTRODUCTION

Time-dependent approaches for describing quantum dynamical processes have been growing rapidly over the past decade due to the computational advantages these methods offer compared to the time-independent methods. Obtaining the information of a molecular process in time domain requires integrating the Schroedinger equation in a large Hilbert space.[1] Exact methods require large basis sets which grow exponentially with the size of the system and hence it is desirable to develop and test approximate methods. Several such methods have been discussed in literature.[2-5] Among the available approximate methods perturbation theory enjoys a pre-eminent position.

In the conventional approach to the perturbation theory, the time evolution operator is expanded as power series in terms of the interaction hamiltonian. In such an expansion, the approximate evolution operator obtained by truncating the series is not always unitary. For developing unitary approximations to the evolution operator the exponential ansatz is very appropriate. In this approach the evolution operator U_F is parametrized as

$$U_F(t) \quad - \quad \exp\,[A(t)]. \qquad (2.1.1)$$

Here A is evaluated perturbatively instead of U . In addition, A is constrained to remain antihermitian at each order, thus guaranteeing an unitary evolution operator irrespective of the order of truncation in A. A perturbation theory based on the above prescription is termed as the Magnus expansion.[6-9]

Several authors discussed the validity of Magnus

expansion.[10"1] The Magnus expansion is subject to two major limitations. First, the theory is essentially perturbative, since the governing equation for the generator A obtained from the Schroedinger equation

$$iU^{-1}\dot{U} = U^{-1}HU \,, \qquad (2.1.2)$$

contains infinite order polynomials in A. Consequently no non-perturbative solution is possible in practice. Second, under certain exotic conditions, even the existence of the solution to that equation is questionable. ' In addition to these formal problems, the Magnus expansion breaks down (as does any perturbative expansion) when some of the unperturbed wave functions are degenerate. To avoid this, degenerate perturbation theories have been developed.[24] In these approaches a set of quasi-degenerate states is defined as a model space and an effective hamiltonian is posited that generates the dynamics of the projection of the exact wave function in the model space. A wave operator is invoked to map the model space component to the exact wave function. Perturbation theory is now applied to the wave operator, while the couplings within the model space are treated exactly. It is possible to modify the Magnus expansion to provide such an effective hamiltonian. The resulting theory has an appearance very similar to canonical van Vleck perturbation theory.[25] However, it is also subject to the same deficiencies of the original formulation.

In view of the above considerations it is desirable to develop alternate perturbation theories for model space effective

hamiltonians based on exponential ansatze. Such a theory should be free from any questions regarding the existence of solution. In addition, the equations for the generators of such a theory should be finite order polynomials, so that a non-perturbative solution is possible (if necessary). The earliest attempts to eliminate the existence problems are due to Wei and Norman. These authors parametrized the time evolution operator in a non-canonical product of exponential operators:

$$U_F = \prod \exp(g_k A_k) . \qquad (2.1.3)$$

The time-dependent complex functions g are determined by a set of nonlinear differential equations obtained by substituting ansatz (2.1.3) into eq. (2.1.2). The operators A_k are the generators of the Lie algebra to which the hamiltonian belongs. Wei and Norman have shown that when the Lie-algebra to which the hamiltonian belongs is a solvable algebra, it is possible to choose the sequence of operators in eq.(2.1.3) such that a global solution to U can be obtained.[18] In addition, they have developed a reduction principle to disentangle the equations of motion of different sets of coefficients when the Lie algebra in question is not simple.[19] The projection operator algebra that we use is a simple algebra and hence cannot be subjected to their analysis. Not withstanding this, it is possible to parametrize the evolution operator in a product form such that a limited version of reduction principle is available in that the equation of motion of different groups of coefficients are decoupled from each other and contain finite order polynomials only. In addition the existence of the solution to these equations can be proved

rigorously. This part of the theory is presented in sec. 2.2.2 in the context of quasi-degenerate perturbation theory after a review of the elements of the requisite effective hamiltonian theory for model spaces in sec. 2.2.1 We then consider three different methods to generate approximations to these equations in sec. 2.2.1 and assess their relative merits. We have applied our methodology to a harmonically driven Morse oscillator with a view to understand the characteristic convergence pattern of these methods and the results obtained are discussed in sec.2.3. We have presented our conclusions in sec. 2.4.

2.2. METHODOLOGY

2.2.1. Effective hamiltonian and model space dynamics:

We assume that the state of the system whose dynamics are to be described is an element of a finite dimensional vector space spanned by the basis functions $\{ |n\rangle, 1 \leq n \leq N \}$. The dynamics of a system are often confined to a small subspace and the states involved in this space require exact treatment while the rest of the states mix only weakly with the manifold of the strongly interacting states. Accordingly we partition the Hilbert space into two orthogonal subspaces: Model space M, consisting of the strongly interacting states characterized by the projection operator P and the remaining states spanning the virtual space V, (projection operator Q).

We now focus our attention on a nonstationary state ψ that was constructed as a superposition of the model space

functions alone at some initial time,

$$\psi(0) = \sum_{n\in M} c_n |n>, \qquad \textbf{(2.2.1a)}$$

and evolves in time according to the Schroedinger equation

$$i\dot{\psi} = H\psi. \qquad (2.2.1b)$$

Our desire is to define a model space effective hamiltonian H_M such that the evolution of the model space component $\phi(t)$ of $\psi(t)$ is described via an equation of motion of the form

$$i\dot{\phi} = H_M \phi. \qquad (2.2.2a)$$

$$\phi(t) = P\psi(t) = \sum_{n\in M} c_n(t)|n>, \qquad (2.2.2b)$$

With this goal in mind, we define a common wave operator[24] U for all the states in M. Thus,

$$\psi(t) = U(t)\phi(t). \qquad (2.2.2c)$$

From eq. (2.2.1b) and (2.2.2c) it follows that ϕ satisfies

$$i\dot{\phi} = \bar{H}\phi, \qquad (2.2.3a)$$

$$\bar{H} = U^{-1}HU - iU^{-1}\dot{U}. \qquad (2.2.3b)$$

Comparing eq. (2.2.2a) and (2.2.3a) we find

$$H_M = P H P. \qquad (2.2.3C)$$

The function $<p$ evolve within the model space as long as

$$Q H P = 0 \qquad (2.2.3d)$$

is satisfied and the initial conditions are specified by eq. (2.2.1a). Consequently, the governing equation for U is given by

$$Q (U^{-1}HU - iU^{-1}\dot{U}) P = 0. \qquad (2.2.3e)$$

Note that eq. (2.2.3d) serves to define the coefficients of only such operators in U which induce transitions from **the** model space to virtual space. The coefficients of the rest of the operators are indeterminate, and as it turns out, irrelevant. Additional conditions can be imposed on H to determine U more fully such as, for example

$$P H Q = 0, \qquad (2.2.3f)$$

which then allows the determination of coefficients of operators which induce transitions from the virtual space to the model space. However, as long as eq. (2.2.3e) is exactly satisfied, these additional conditions have no influence on H_M as we shall demonstrate in sec. 2.2.3.

In most practical calculations one is more interested in the full wave function or expectation values of the dynamical variables rather than the projection of the wave function onto the model space. The full wave function is obtained by operating on ϕ

by U. We now turn to the calculation of physically relevant expectation values. The expectation value of a dynamical variable 0 is given by

$$< 0 > = < \psi \backslash 0 \backslash \psi > = <\phi|U^{+}OU|\phi>. \qquad (2.2.4a)$$

With ϕ and U obtained from eq. (2.2.2a) and eq. (2.2.3e) respectively, this provides a straight forward procedure. An alternative procedure, more in the spirit of the effective operators in the model space is the following. We define an auxiliary bra function $< \phi |$ by

$$< \phi| = < \text{tfrlU}. \qquad (2.2.4b)$$

From the Schroedinger equation for $< \psi|$

$$-i < \psi| = < \psi|H. \qquad (2.2.4c)$$

We get the working equation for $< \phi|$ as

$$-i < \phi| = < \phi|H, \qquad \textbf{(2.2.4d)}$$

where H is defined as before. The expectation value of 0 is now given by

$$< 0 > = < \psi |O| \psi > = < \phi |O| \phi >, \qquad (2.2.4e)$$

where

$$\bar{O} = U^{-1}O U. \qquad (2.2.4f)$$

Here $\bar{O}$ is the model space effective operator corresponding to 0 in the full Hilbert space. This result holds irrespective of whether

U is unitary or not. One noteworthy point here is that $\langle\bar{\phi}|$ is not the complex conjugate of $|\phi\rangle$, but must be evolved independently according to eq. (2.2.4d). In general, $\langle\phi|$ is not confined to the model space. However, if eq. (2.2.3f) is imposed in addition to eq. (2.2.3d) while determining U, $\langle\phi|$ would also be confined to the model space.

2.2.2. Operator algebra and the evolution operator:

We now turn to the construction of the model space wave operator U. The set of operators that act on the vector space of functions is a complete set and is spanned by the basis set of the generators of the unitary group, $L = \{|i\rangle\langle j|, 1 \leq i,j \leq N\}$. This operator set is closed under commutation, thus forming a Lie algebra. The hamiltonian, given by

$$H = \sum_{i,j} h_{ij} |i\rangle\langle j| \qquad (2.2.5)$$

is an element of this Lie algebra. Given that the hamiltonian is an element of the algebra, the full evolution operator U_F can be parametrized, at least locally, as

$$U_F = \exp\left[\sum_{i,j} f_{ij}(t)\, |i\rangle\langle j|\right], \qquad (2.2.6a)$$

and satisfies the Schroedinger equation

$$i\dot{U}_F = HU_F. \qquad (2.2.6b)$$

eq. (2.2.6a) is the starting point for the Magnus expansion

approach.[6"'] An alternative form is to write U as a product of exponentials (the so called Wei-Norman form) rather than a single exponential,[18,21]

$$U_F = U_1 U_2 U_3 \cdots, \tag{2.2.7}$$

where each U_i is an exponential operator. Wei and Norman and more recently Wolf and Korsch[21] have discussed a reduction principle to obtain a convenient sequence of U_i when the algebra is semisimple. In addition Wei and Norman has shown that for solvable Lie algebras there exists a basis and an ordering of the basis for which the product form is global. Since the only invariant subalgebras of the projection operator algebra are the null set and itself, the algebra is simple and hence this procedure cannot be used here. However, it turns out that a limited form of a reduction principle is possible in this case also due to the special structure of the algebra. To exhibit this structure we classify the operator set as follows:

set of excitation operators: $E = \{ X = |v\rangle\langle m| \; ; \; v \in V, \; m \in M \}$
set of deexcitation operators: $D = \{ Y = |m\rangle\langle v| \; ; \; v \in V, \; m \in M \}$
set of shift operators: $S = \{ Z = |m\rangle\langle n|, \; W = |u\rangle\langle v| \; ; \; m,n \in M ; \; u, v \in V \}$.

These operators satisfy the following commutation relations:

$$[X,X] = [Y,Y] = 0, \tag{2.2.8a}$$

$$[X,Y] = Z + W, \tag{2.2.8b}$$

$$[X,Z] = X = [X,W], \tag{2.2.8c}$$

$$[Y,Z] = Y = [Y,W]. \tag{2.2.8d}$$

Note that each of these sets defines a **subalgebra** of L. In addition S ∪ E and S ∪ D are also closed under **commutation.** We now note that (a) the excitation operators in H can be eliminated by a **similarity transformation** generated by X alone: Consider **the parametrization**

$$U_F = U_X U_R, \tag{2.2.9a}$$

$$U_X = \exp(X). \tag{2.2.9b}$$

The equation of motion for U_R is given by

$$i\dot{U}_R = H_R U_R, \tag{2.2.9c}$$

$$H_R = U_X^{-1} H U_X - i U_X^{-1} \dot{U}_X. \tag{2.2.9d}$$

In other words, U_R is generated by the effective hamiltonian operator H_R. It is possible to eliminate all X operators in H_R by requiring

$$Q \left(U_X^{-1} H U_X - i U_X^{-1} \dot{U}_X \right) P = 0, \tag{2.2.9e}$$

which provides the working equation for U_A. (b) If the effective hamiltonian operator H_R does not contain X operators then U_R can be parametrized as

$$U_R = \exp [Y+Z+W], \tag{2.2.9f}$$

since S ∪ D is a Lie algebra and H_R **belongs to it. Combining**

these two statements, and invoking similar arguments with respect to the deexcitation operators, we arrive at

$$U_F = \exp(X)\exp(Y)\exp(Z+W). \tag{2.2.10}$$

Thus the model space wave operator U is given by

$$U = \exp(X)\exp(Y), \tag{2.2.11}$$

since the effect of Z can be absorbed into ϕ and W acting on the model space gives zero. The generators X and Y satisfy

$$iX = Q \exp(-X)\ H \exp(X)\ P, \tag{2.2.12a}$$

$$iY = P \exp(-Y)\ [\ \exp(-X)H\exp(X)-iX\ ]\ \exp(Y)\ Q. \tag{2.2.12b}$$

These equations are decoupled since the governing equation for X does not depend upon Y. In this sense we have obtained a reduction of the operator set. Let us note that any other ordering of operators (e.g. exp(Z)exp(X)exp(Y)exp(W)) does not lead to decoupled sets of equations.

2.2.3. Perturbation theory:

We now turn to the explicit solution of eq.(2.2.12). From eq. (2.2.12a) we obtain by Hausdorff expansion

$$\begin{aligned} i\dot{X} &= Q\ (H + [H,X] + 1/2!\ [[H,X],X])\ P, \\ &= H_{QP} + H_{QQ}X - XH_{PP} - XH_{PQ}X. \end{aligned} \tag{2.2.13a}$$

This equation is a matrix Ricatti equation and is the result of a multistate generalization of the nonlinear quotient approach discussed by Dion and Hirschfelder.[29] The existence theorem proved in that context (theorem 9 of ref. 29) holds here also. Since X is a vxm matrix operator where v and m are the dimensions of the V and M respectively, parametrizing X formally as

$$X = FG^{-1} \tag{2.2.13b}$$

where F is a vxm matrix and g is a mxm matrix and substituting it into eq. (2.2.13a) we obtain

$$i\dot{F}G^{-1} - iFG^{-1}\dot{G}G^{-1} = H_{QP} + H_{QQ}FG^{-1} - FG^{-1}H_{PP} - FG^{-1}H_{PQ}FG^{-1}. \tag{2.2.13c}$$

This equation can now be decoupled into two sets by writing

$$i\dot{G} = H_{PP}G + H_{PQ}F, \tag{2.2.13d}$$

$$i\dot{F} = H_{QP}G + H_{QQ}F. \tag{2.2.13e}$$

Note that eq. (2.2.13d) and eq.(2.2.13e) recover the original Schroedinger equation. The initial condition

$$X(0) = 0 \tag{2.2.13f}$$

is satisfied by requiring

$$F(0) = 0, \tag{2.2.13g}$$

$$G(0) = 1 \tag{2.2.13h}$$

without loss of generality. The solution to X exists as long as G

is non-singular. Note that from eq. (2.2.13) G represents the matrix of the projections of all linearly independent states that were started at t = 0 in the model space. Thus G becoming singular implies that two or more such states have evolved in such a way that their projections in the model space at this point of time are linearly dependent. In such a situation X does not have any meaningful solution. Except in such pathological cases, X has a global solution. In a similar fashion, it can be shown that eq. (2.2.12b) for Y also has a global solution under the same conditions.

Since the multicommutator expansion in eq. (2.2.13a) is finite, a nonperturbative solution for X is possible in contrast to Magnus expansion. In addition, a perturbative expansion for X by this approach has far fewer terms at any order compared to its counterpart by Magnus expansion.

Expanding X perturbatively we obtain

$$X = \sum_n \lambda^n X_n, \tag{2.2.14a}$$

$$i\dot{X}_n = H_{QP}\delta_{n1} + H_{QQ}X_{n-1} - X_{n-1}H_{PP} - \sum_{r=1}^{n-2} X_r H_{PQ} X_{n-r-1}, \tag{2.2.14b}$$

where n is the order of perturbation. The model space effective hamiltonian (eq. (2.2.2b)) becomes

$$H_M = H_{PP} + H_{PQ}X - Y(H_{QP} + H_{QQ}X - XH_{PP} - XH_{PQ}X - i\dot{X}). \tag{2.2.15a}$$

If X satisfies eq. (2.2.13a) exactly, this reduces to

$$H_M = H_{PP} + H_{PQ}X. \tag{2.2.15b}$$

This is expected since the action of Y on the model space gives zero. Consequently these operators should have no influence on the model space dynamics. Thus a simple minded perturbation theory consists of two steps: (1) Solve eq.(2.2.14b) to some finite order. (2) Construct H_M according to eq.(2.2.15b) and integrate eq. (2.2.2a) for ϕ. We shall refer to this approach as the similarity transformation based perturbation theory (STP), since in effect, it postulates U = exp(X).

One possible problem with STP is that, in the strong coupling regime the perturbative dynamics may not conserve the norm of the wave function. This is the well known problem of intruder states.[24] When eq. (2.2.3d) is satisfied, these states have no influence on the model space dynamics because, any vector from the model space would evolve within the model space as long as $H_{OP} = 0$. If X is obtained from perturbation theory, eq. (2.2.3d) is violated. In such a case, invocation of eq. (2.2.15b) is equivalent to replacing H in eq. (2.2.3b) with H_A such that

$$H_A = H - R, \tag{2.2.16a}$$

where

$$Q R P = Q H P. \tag{2.2.16b}$$

The hamiltonian corresponding to H_A in the full Hilbert space is

$$H = H - URU^{-1}. \tag{2.2.17}$$

If the H operator is non-hermitian, it could, in the course of its evolution, develop complex eigenvalues. The eigenvectors associated with these eigenvalues are the intruder states. When the intruder states develop a large component in the

model space at some stage, the model space states would grow exponentially. Such a situation can be expected when the states in the model space interact strongly with the virtual space.

There are two ways to eliminate the influence of the intruder states. The first approach is to expand the model space to incorporate all the strongly interacting states as advocated by Jolicard and Grosjean.[24] This forms the basis of the intermediate hamiltonian approach discussed in the context of the usage of incomplete model spaces along with the coupled cluster method for stationary states.[28] A second approach is to ensure that H is hermitian through out the course of the evolution. Note that only the QP block of the R operator is specified by eq.(2.2.16b). It is possible to use this flexibility to ensure a hermitian H. Essentially H is hermitian if R = URU is hermitian. Thus, in terms of the sub-blocks of the R operator the following equations must be satisfied to guarantee the hermiticity of H:

$$\bar{R}_{QQ} = R_{QQ} + XR_{PQ} = \bar{R}^{+}_{QQ}, \tag{2.2.18a}$$

$$\bar{R}_{PP} = R_{PP} - R_{PQ}X = \bar{R}^{+}_{PP}, \tag{2.2.18b}$$

$$\bar{R}_{PQ} = R_{PQ} = \bar{R}_{QP}{}^{+}. \tag{2.2.18c}$$

Since R_P, R_{PQ} and R are not defined by eq. (2.2.16b) additional conditions can be imposed. For example setting

$$\bar{R}_{PQ} = R_{PQ} = R_{PP} = 0, \tag{2.2.19}$$

we arrive at

$$\bar{R}_{PP} = 0, \qquad \textbf{(2.2.20a)}$$

$$\bar{R}_{QP} = (R_{QP} - R_{QQ}X) = 0. \qquad \textbf{(2.2.20b)}$$

Thus choosing an R_{OO} such that $R = R_{OC}$ and requiring $R_{OP} = R_{OO}X$ would guarantee that H is hermitian. In such a case X must satisfy

$$i\dot{X} = H_{QP} + (H_{QQ} - R_{QQ})X - XH_{PP} - XH_{PQ}X. \qquad \textbf{(2.2.21)}$$

In this case X can not be obtained as a power series. Instead approximations to X are obtained by defining different R_{OO} matrices. We term approaches based on eq. (2.2.21) as the hermitised similarity transformation (HST) based theories.

An alternative approach to avoid norm violations is to insist that the full evolution operator of eq. (2.2.10) underlying the model space evolution operator to be unitary. It can be shown by direct substitution that U_F is unitary if Y,Z and W satisfy the following equations:

$$Y = - (1+X^{+}X)^{-1} X^{+}, \qquad \textbf{(2.2.22a)}$$

$$Z = - 1/2 \ln (1+X^{+}X), \qquad \textbf{(2.2.22b)}$$

$$W = - 1/2 \ln (1+XY). \qquad \textbf{(2.2.22C)}$$

Thus, usage of eq. (2.2.15a) with eq. (2.2.22a) for Y ensures that there is no norm violation. This approach will be called as the unitary transformation based perturbation theory (UTP) in the following. In the next section we study the numerical performances of these three methods.

2.3. MODEL APPLICATIONS

To examine the relative performances of the three approaches described in the previous section and also to gain an understanding of their convergence properties we have used the three approaches to follow the dynamics of a harmonically driven Morse oscillator. The hamiltonian of the system is given by

$$H = H_0 + V, \tag{2.3.1}$$

$$H_0 = p^2/2m + D(1-e^{-\alpha x})^2, \tag{2.3.2a}$$

$$V = A_0 x \cos(\omega t). \tag{2.3.2b}$$

The parameters D, α, and m were chosen to correspond to that of HF molecule and are collected in Tab. 2.1.[22] A was chosen such that the intensity of the external field was in the range of 1 to 2 TW/cm^2.[23]

Table 2.1 Morse parameters for HF.

Parameter	Value
D	6.125 ev
α	1.1741 a_0^{-1}
M_H	1.00797 amu
M_F	18.9984 amu

In all the calculations presented below the frequency of the radiation field was set to be in 1:1 resonance between ground and the first excited states. Consequently, these two states are degenerate and interact strongly, while the coupling to the rest

of the states is taken to be weak enough to be subjected to a perturbative treatment. Thus all the perturbative calculations were carried out in the interaction picture with a model space spanning the ground and first excited states and the lowest ten eigenstates of the Morse oscillator were used to define the complete vector space.

In the Figure 2.1 we plot the expectation value of the unperturbed Morse oscillator calculated by STP as a function of time when the intensity of the driving field is 1 TW/cm (A = 0.04503 eV/a). Since the Y operators are not evaluated in STP the expectation values were obtained by eq. (2.2.4a). It appears that the first order theory fails to improve upon the zeroth order description but 3rd and 5th orders are practically indistinguishable and quite close to the exact results indicating that the perturbation series seems to be convergent at this intensity at least over the time period that has been studied.

In Fig. 2.2 we plot the expectation value of the unperturbed hamiltonian of the Morse oscillator calculated by STP as a function of time when the intensity of the driving field is 2 TW/cm . Upto about 15 optical cycles (o.c.) the perturbation theory provides an improvement over the zeroth order description with the accuracy of the perturbation solution improving with increasing order. Beyond that the energy calculated by all the orders blows up indicating the divergent nature of the perturbation series.

In Fig.2.3 we plot the expectation value of position as a function of time by STP at the field intensity of $2TW/cm^2$. Beyond 10 optical cycles first order result starts deviating from the

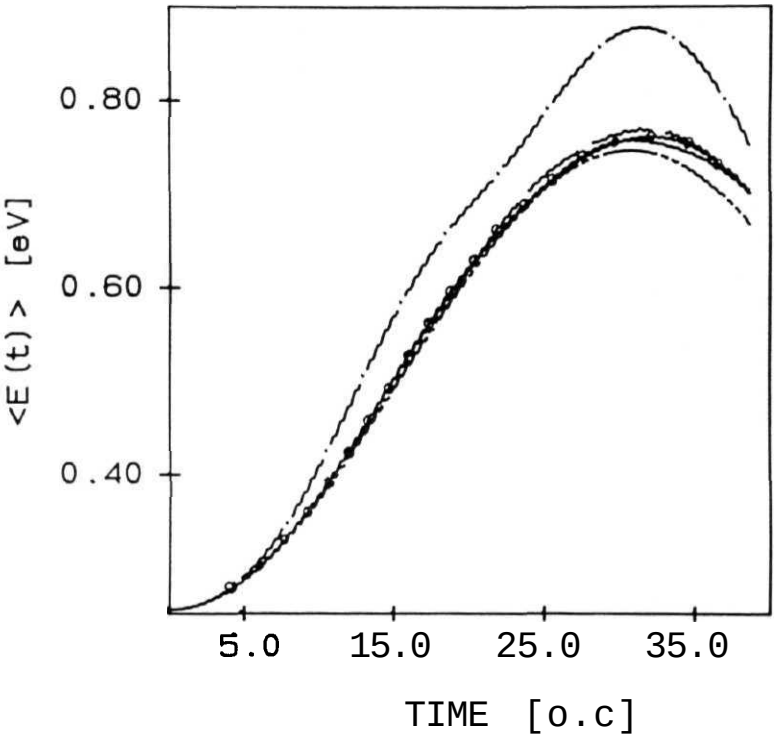

Fig.2.1 Energy of the Morse oscillator as a function of time with the field intensity I = 1.0 TW/cm by STP. Continuous line with circles: Converged basis set calculation. Dash and double dotted line: Basis set restricted to two functions. Dash and dotted line: First order. Dashed line: third order. Continuous line: Fifth order.

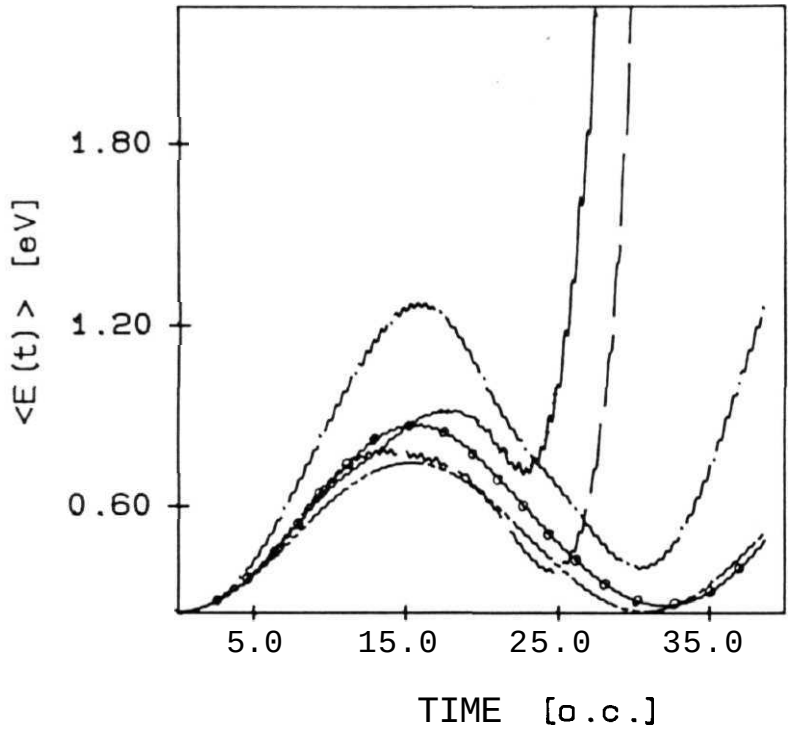

Fig.2.2 Same as Fig. (2.1) but at the field intensity of 2 TW/cm . Figure conventions are the same as before.

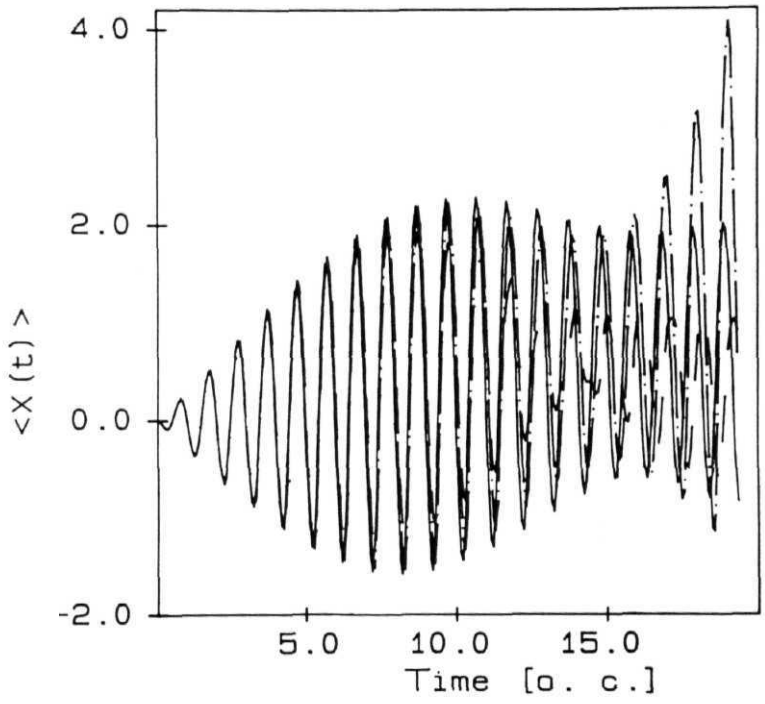

Fig.2.3 Position expectation values as a function **of time at the** field intensity same as Fig. (2.2) by STP. Continuous line: Converged basis set calculation. Long dahes: First order. Dash and dotted line: Third order.

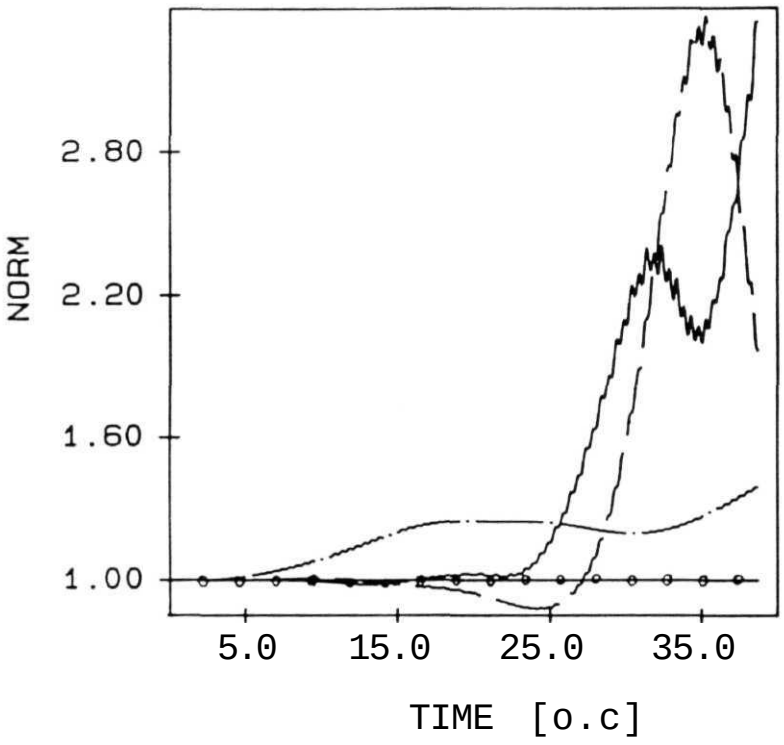

Fig. 2.4 Norm of the perturbed wave function at I = 2 TW/cm Figure conventions are the same as in Fig.(2.1).

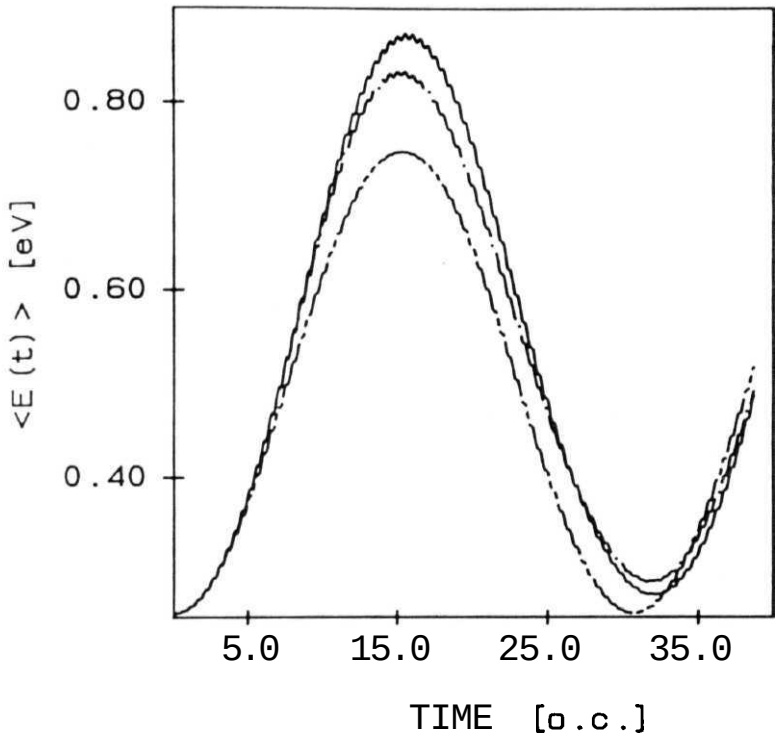

Fig. 2.5 Energy of the Morse oscillator as a function of time by HST. Continuous line: Converged basis set calculation. Dash and double dotted line: Basis set restricted to two basis functions. Dash and dotted line: HST calculation.

exact values. The third order calculation is an improvement over the first order result. In the case of position expectation values also the accuracy is improving with the increase in the perturbation order.

The divergent nature of the perturbation theory indicated by Fig.2.2 and 2.3 is reinforced by Fig. 2.4 in which norm of the perturbed wave function defined by

$$N = < \phi | \exp(X^{+}) \exp(X) | \phi >^{1/2} \qquad (2.3.3)$$

is plotted as a function of time. It appears from this that the higher the order of the perturbation theory the later is the occurrence of the norm violation. But once the norm violation begins it appears to grow faster in higher order approximations.

In Fig.2.5 we present a similar calculation to Fig.2.2 but based on HST in which we have set $R = H_{OO}$. This is equivalent to solving the equation

$$iX = H_{QP} - XH_{PP} - XH_{PQ}X \qquad (2.3.4)$$

for X. This is a nonperturbative approximation and as may be expected performs quite satisfactorily.

In Fig. 2.6 the energy expectation value calculated by the UTP approximations is plotted as a function of time at the same intensity as Fig.2.2. Here the expectation values were obtained by using eq. (2.2.4f) . In the early phase of the time development (upto about 20 o.c.) the approximation based on the unitary transformation is far worse than the corresponding STP

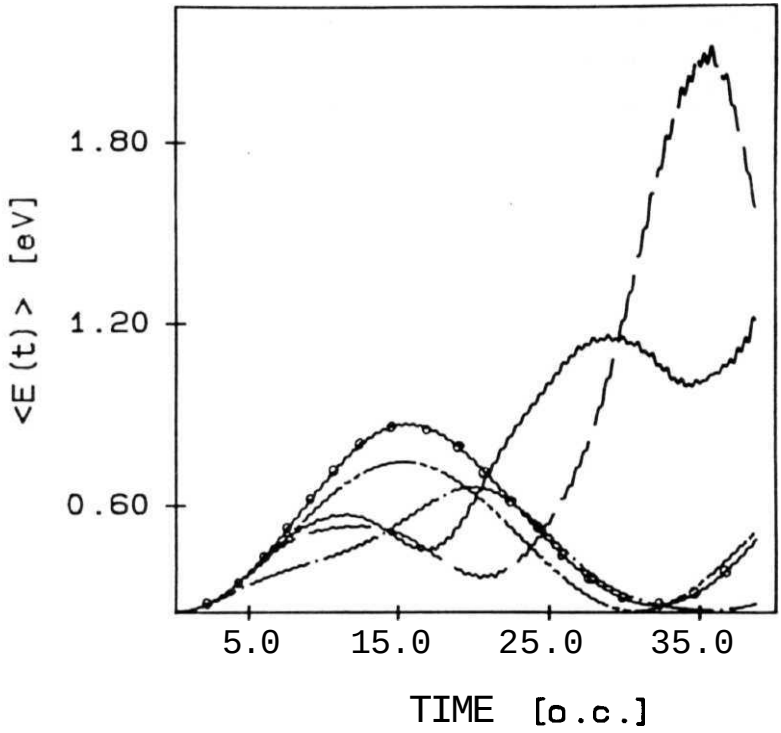

Fig. 2.6 Energy of the Morse oscillator as a function of time with the field intensity I = 2.0 TW/cm^2 by UTP. Figure conventions are the same as in Fig. (2.1).

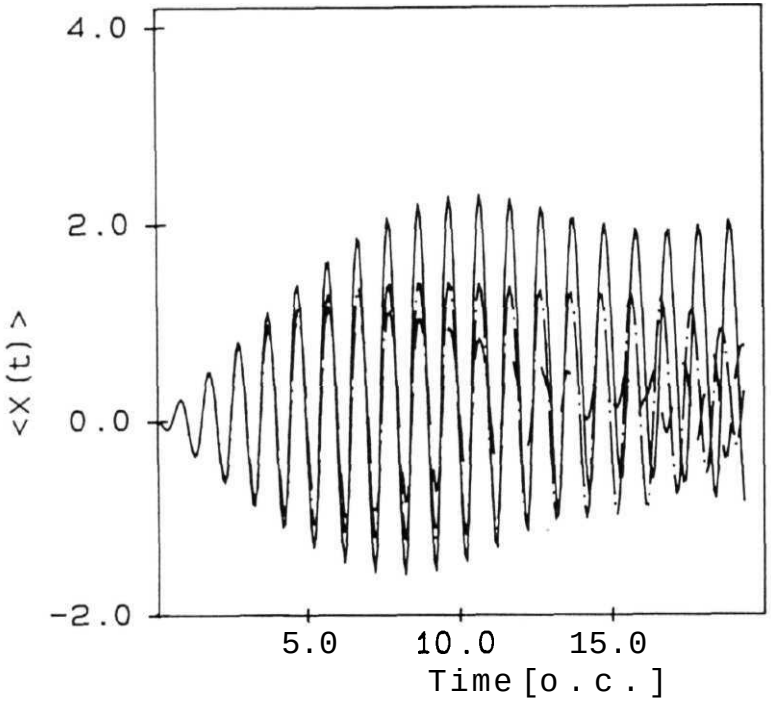

Fig.2.7 The position expectation value as a function of time by UTP at the field intensity I = 2.0 TW/cm^2. Figure conventions are the same as in Fig.(2.3).

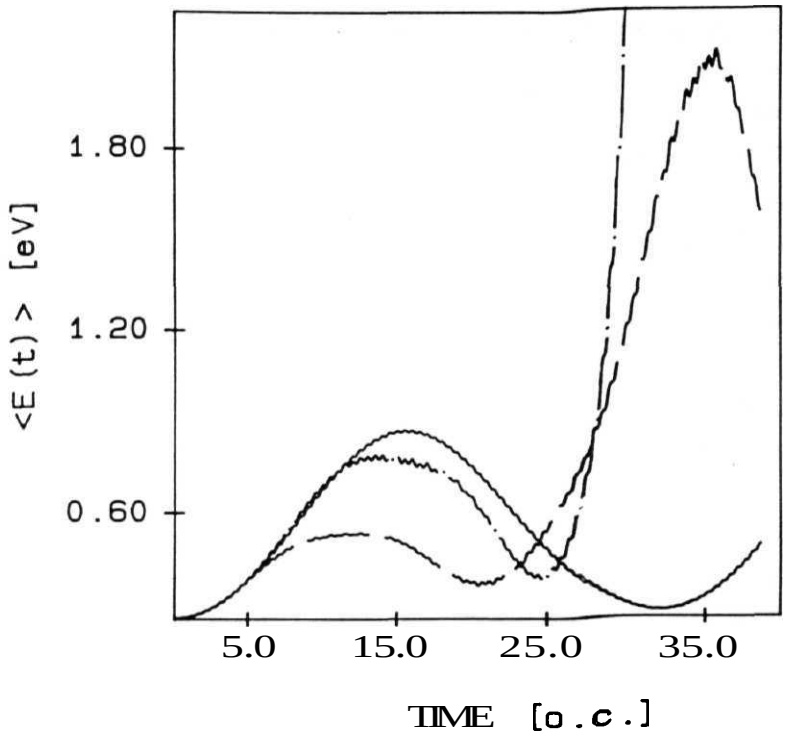

Fig. 2.8 Comparision of STP and UTP values of energy of the Morse oscillator. Continuous line: Converged basis set calculation. Dashed line: Third order UTP. Dash and dotted line: Third order STP.

version. However, since there is no norm violation in this approach its validity improves at longer times when the approximations based on the STP breakdown due to norm violations. However these approximations seem to be worse than the hermitised version. Similar trends are observed even in the case of position expectation values as a function of time by UTP which are plotted in Fig. 2.7.

Comparing the energy expectation values obtained from STP and UTP approaches (Fig. 2.8), it appears that the result of STP version is close to exact result up to about 20 o.c.. Beyond that it diverges. The UTP version underestimates the energy at least in the initial phase. The explanation for this can be given as follows: Substituting for Y in eq. (2.2.15a) results in the equation

$$H_M = (1+X^+X)^{-1} (H_{PP} + H_{PQ}X + X^+H_{QP} + X^+H_{QQ}X - iX^+X). \qquad (2.3.5)$$

It can be seen from this equation that when a particular X value turns out to be large, the corresponding value of the factor $(1+X^+X)$ will be very small, consequently the matrix elements in the corresponding row of H_M become negligible. This means, the model space state which is strongly interacting with the virtual space is being eliminated from the model space for all practical purposes. In effect then the model space is reduced to one function and the wave packet is unable to gain energy.

2.4. CONCLUDING REMARKS

Degenerate perturbation theory is a convenient tool for

the description of dynamics of systems with a large number of strongly interacting states. Any approach to such a perturbation theory defines a common wave operator for all the states in the model space.[24] In this work we have studied the development of three such approaches based on exponential ansatze. We have opted for Wei-Norman type of product form for the time evolution operator rather than a single exponential type normally invoked in the Magnus expansion. Based on the structural properties of the Lie algebra under consideration we have shown that the evolution operator is partially reducible in the sense that the computation of the time-dependent coefficients associated with the excitation operators is decoupled from the computation of the rest of the operators. More generally, if the algebra L underlying the dynamics can be decomposed into a sequence of subalgebras L_k such that

$$L = L_0 \supset L_1 \supset L_2 \supset \ldots , \qquad (2.4.1)$$

then, parametrization of U as

$$U = \exp(X_0)\exp(X_1)\exp(X_2)\ldots ; \quad X_k \in L_k - L_{k-1} \qquad (2.4.2)$$

leads to decoupling of the equations of motion for different X_k. A perturbation theory based on such decouplings has the advantage that it requires less computational effort than the Magnus expansion. First, the equations for different generators are decoupled, and consequently the original problem is broken down into several subproblems which can be solved sequentially. Second, since the equations for the generators contain finite order polynomials, the number of terms at each order of perturbation theory are fewer than in the corresponding Magnus

expansion. Lastly, the resulting equations provide a global solution to the wave operator. We note in passing that algebraic methods have been used in the past to provide approximate solutions to the Schroedinger equation.[4''] In all these approaches the hamiltonian is not in general an element of the algebra used. Consequently, the algebraic approach does not provide the complete solution. Instead it is used to construct a convenient time dependent coordinate system in which a basis set is defined to carry out the dynamical calculations. The most commonly used algebras in this context are the harmonic oscillator algebra and its multidimensional extensions. Because of the nonlinearities in the equations of motion for the generators, these approaches are also subject to the question of the existence of the solution depending on the order of the operators used. However, the harmonic oscillator algebra is a semisimple algebra and can be treated on the lines discussed by Wolf and Korsch.[21] A particularly well developed approximation method based on this approach is the time-dependent rotated Hatree method discussed by Kucar et al,[5] who also prove the existence of a global solution when a particular ordering of the operators is chosen. However all these approaches differ from ours because we work with the algebra that contains the hamiltonian. The work of Mukherjee[28] is closest in spirit to ours, in that he uses an exponential ansatz for the full evolution operator which he then factorises into the model space wave operator and the closed part containing the norm and the phase corrections. However, his ansatz is motivated by the requirements of the asymptotic separability. In our case the factorisation of the excitation and shift operators (open and

closed operators in the terminology of Mukherjee) is a consequence of the structure present in the algebra.

While the decoupling of equations of motion provide significant formal advantages as discussed above, in an approximate calculation they could lead to norm violations because the effective hamiltonian underlying specific approximations in the full Hilbert space could become nonhermitian. Analyzing the source of such nonhermiticity we found criteria by which an approximation could be tested a *priori* as to whether it would lead to norm violation or not. Alternatively, the model space wave operator could also be designed such that the full evolution operator from which it is generated is unitary.

We have studied the performances of these three methods in a model system. It appears from these studies that the perturbation theory based on similarity transformation seems to be adequate at least for weak coupling or short time dynamics while at longer times the norm violation effects seem to be predominant. We have also tested a nonperturbative approximation which was guaranteed to conserve the norm. The performance of this approximation was quite good. Approximations based on unitary transformation do not suffer from norm violation; however, this seems to be achieved at the cost of practically eliminating some of the states from the model space. Its performance is in general worse than an unconstrained similarity transformation based approach. These conclusions are, ofcourse, tentative and would have to be backed up by more extensive studies on these approaches.

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CHAPTER III

LIE-ALGEBRAIC STRUCTURE AND COUPLED CLUSTER METHOD

3.1. INTRODUCTION

In the previous chapter, we were concerned about the development of quasi-degenerate perturbation theory for the calculation of quantum dynamics in the Hilbert spaces. The calculation of time evolution is carried out in two parts in this approach. A group of strongly interacting states is identified as the model space. The dynamics of the wave packet in the model space is treated exactly. The effect of the virtual space is then treated perturbatively. To this end, the evolution operator U is factorised as

$$U_F = U U_M. \qquad (3.1.1)$$

Here the model space evolution operator U describes the dynamics of the projection of the wave packet in the model space (eq.(2.2.2b))

$$\begin{aligned} \phi(t) &= P \psi(t) \\ &= U_M(t) \phi(0). \end{aligned}$$

It is generated by model space effective hamiltonian H (eq.(2.2.3a))

$$i \dot{U}_M = H_M U_M,$$

where the effective hamiltonian is defined as (eq.(2.2.3c))

$$H_M = P (U^{-1} H U - i U^{-1} \dot{U}) P.$$

To ensure that ϕ is confined to the model space (eq.(2.2.3d))

$$Q\,(U^{-1}HU - iU^{-1}\dot{U})P = 0$$

must be satisfied. Q and P are the projection operators onto the virtual and model spaces respectively.

An exponential ansatz is posited for the wave operator U. Based on the Lie-algebraic structure present in the operator set, we have showed that the wave operator could be factorised as

$$U = U_x U_y, \qquad (3.1.2)$$

where U_x is generated by the excitation operators alone and the U_y is generated by the deexcitation operators. The equation of motion for U_x does not depend upon the U_y operator. This procedure is essentially equivalent to putting the wave operator in the normally ordered form with respect to the model space, since the deexcitation operators give zero acting on the model space.

In this chapter, we extend the approach to the Fock space. Since Fock space is the union of all the Hilbert spaces with varying number of particles, this provides a convenient approach for analyzing the dynamics of a many body system in terms of the dynamics of the constituent subsystems. This is useful at two levels. At a conceptual level it provides a pictorial view of the dynamics in terms of the subsystems. At a computational level, it allows the definition of computationally tractable nonperturbative approximations in terms of subsystem amplitudes when the actual number of degrees of freedom is large. The

guiding principle for constructing the wave operator, once again is the sub-algebraic structure present in the set of operators active in the Fock space. It turns out that this analysis leads to the time-dependent generalization of the multireference coupled cluster methods developed earlier in the context of electronic structure theories.

The coupled cluster method (CCM) is currently one of the most popular computational tools for performing size extensive energy calculations for many electron systems. This method uses exponential ansatze to generate the correlated N-electron wave function with the reference wave function taken most often in the form of a single Slater determinant. Generalization of the single reference CCM methods consider a manifold of states (spanning the model space) and posit an effective hamiltonian H_{-} in that space whose eigenvalues correspond to some of the (desired) eigenvalues of the original hamiltonian. These multireference coupled cluster methods (MRCCM) can be classified into two classes[6] : (a) the Fock space MRCCM and (b) the Hilbert space MRCCM. The Fock space MRCCM postulates a valence-universal wave operator fi to map the reference states to the corresponding correlated states in that it requires that the same wave operator should correlate the reference states of N±l, N±2 particle systems generated by deleting or adding the appropriate number of particles from the states in the N-particle model space. Various Fock space methods have been discussed in literature.[6] These differ principally in their choice of the actual form of the wave operator.

An important ingradient of the Fock space MRCCM is the subsystem embedding condition. According to it, the cluster

operators corresponding to an m-valence system do not influence the cluster operators corresponding to an n (<m) particle system. This leads to a significant reduction in the computational effort. This was originally postulated as an additional condition along with a multiple cluster ansatz for the wave operator.[14] Later Hague and Mukherjee[4] have shown that this holds rigorously when the wave operator is taken to be a normally ordered exponential ansatz.

Once the form of the wave operator is chosen, there are two possible ways to generate the CCM equations. In the first approach, termed the similarity transformation based approach, the effective hamiltonian is defined as

$$H_{eff} = \Omega^{-1} H \Omega. \tag{3.1.3}$$

The cluster matrix elements are chosen such that the functions in the model space are decoupled from the rest of the Hilbert space.

$$QH_{eff}P = 0. \tag{3.1.4}$$

The model space effective hamiltonian is then simply $PH_{eff}P$.

In the second approach, the Bloch equation is invoked to determine both Ω and H_{eff}.

$$H\Omega P = \Omega P H_{eff} P. \tag{3.1.5}$$

Several ansatze have been posited for Ω. Noteworthy among these are:

(a) The multiple exponential ansatze[14]

$$\Omega = \Omega_0 \Omega_1 \Omega_2 \ldots, \tag{3.1.6a}$$

$$\Omega_i = \exp(S_i). \tag{3.1.6b}$$

(b) The unitary ansatz[8]

$$\Omega = \exp(\sigma), \tag{3.1.7a}$$

$$\sigma = -\sigma^{+} \tag{3.1.7b}$$

$$\sigma_{D} = 0 \text{ (Kemble condition).} \tag{3.1.7C}$$

(c) The normally ordered exponential ansatz[5]

$$\Omega = N[\exp(S)]. \tag{3.1.8}$$

(d) The biexponential ansatz[13]

$$\Omega = \exp(S)\exp(\sigma). \tag{3.1.9}$$

The biexponential ansatz of Arponen[13] is termed the extended coupled cluster method. In its original form it is restricted to single reference states. Its extensions to quasi-degenerate many folds has not been discussed in the literature. As can be seen the wave operator fi of CCM corresponds to the time-dependent wave operator U of eq.(3.1.1). To avoid any mixing up, we continue to use U for the time-dependent wave operator and reserve fi for the time-independent case.

A few authors have discussed the time-dependent generalization of the coupled cluster method[16-22]. Most of these studies considered only systems with single reference state. Arponen[13] also has analyzed the time-dependent version of his extended coupled cluster method. More recently Guha and Mukherjee[21] considered the multireference time-dependent coupled cluster method using the normally ordered exponential ansatz.

In the next section we analyze the subalgebra structure in the Fock space and construct the time-dependent wave operator. It turns out that there are several subalgebra sequences in the Fock space that can be used to decouple the equations of motion for the various generators. We discuss two of them: one of them corresponds to the wave operator advocated in ref.14, while the other gives a multi-reference generalization of the biexponential ansatz originally proposed by Arponen.[13] For simplicity, we assume that the physical system consists of only one type of indistinguishable particles. Extensions to systems containing several types of particles is straight forward. In sec. 3.2 we present the details of the Lie-algebraic structure and the construction of the wave operator and sec.3.3 contains some general remarks.

3.2 LIE-ALGEBRAIC STRUCTURE AND THE WAVE OPERATOR

We begin our construction by specifying the model space. To this end, we classify the single particle states in the usual fashion as hole, valence and particle states. We assume that the hole orbitals are occupied in all the model space determinants and the particle states are always empty while the valence orbitals are occupied in some of the model space determinants. Note that this procedure would generate a sequence of model spaces $\mathbf{M}$ characterized by the projection operator P_n, where n is the number of valence particles. In the terminology currently in vogue, all these are complete model spaces. The corresponding complementary spaces are represented by V_n (projection operator Q_n).

We next turn to the analysis of the operator set that

generates **U.** Since the hamiltonian of a many particle system

$$H = \sum \langle i|h|j\rangle\, a_i^+ a_j + \sum \langle ij|v|kl\rangle\, a_i^+ a_j^+ a_l a_k + \ldots \qquad (3.2.1)$$

commutes with the number operator, only those operators which commute with the number operator contribute to U. We note in passing that the complete set of such operators is closed under commutation and hence forms a Lie algebra $\mathbf{L_o}$. Following Kutzelnigg[8] we classify this operator set as

(i) C : Set of all Closed operators. These contain valence operators only and thus can not induce transitions from M_n to V_n or vice versa. These corresponds to the shift operators of Chapter II.

(ii) B : Set of all operators closed from Below. The ani-anihilation operators here are all either the Valence or hole type. Diagrammatically all the incoming lines are valence lines in these operators. Thus they can cause transition from M to V_n **but not** vice versa. These are analogous to the excitation operators of Chapter II.

(iii) A : Set of all operators closed from Above. These operators are adjoint to B type operators. These can only cause transitions from V_n to M_n. These correspond to the deexcitaton operators.

(iv) 0 : Set of Open operators that do not belong to any of the above sets. They contain active and inactive lines on both sides of the vertex and they **have zero** matrix elements between functions of the model spaces.

We further classify the non-diagonal operators B and A as follows. We define B as the set of B type operators that contain exactly k number of valence and arbitrary number of hole annihilation operators. Thus

$$B = \bigcup B_k, \tag{3.2.2a}$$

$$B_k \cap B_l = 0. \tag{3.2.2b}$$

Similarly we define A as the set of A type operators with exactly k number of valence and arbitrary number of hole creation operators and

$$A = \bigcup A_k. \tag{3.2.3}$$

Our goal is to construct U such that the effective hamiltonian H_{ff} defined by eq.(3.1.3) does not couple functions belonging to M and V spaces. This is equivalent to the statement that H_{ff} does not contain any B type operators. We carry out this construction in a hierarchical manner. In the first step we define

$$U_0 = \exp(S^0), \tag{3.2.4a}$$

$$S^0 = \sum s_I^0 b_I^0 \; ; \; b_I^0 \in B_0. \tag{3.2.4b}$$

We now construct an intermediate operator H_1, via

$$H_1 = U_0^{-1} H U_0 - i U_0^{-1} \dot{U}_0 \tag{3.2.4c}$$

and determine the unknown coefficients s requiring

$$Q_0 H_1 P_0 = 0. \qquad (3.2.4d)$$

This essentially requires that the coefficients of B_0 type operators in H are set equal to zero. Since the number of operators in B equals the number of equations in eq.(3.2.4d) these equations can be solved.

We now note that H belongs to the set of operators $L_1 = L_0 - B_0$. It is easy to show that L_1 is closed under commutation and hence is a Lie algebra. All the operations in L contain at least one valence annihilation operator. Consequently, the commutator of any pair of them would also have at least one valence annihilation operator in it. Thus it cannot belong to the B_0 set.

In the second step we set out to eliminate the B type operators in H_1. To this end we use another operator U_1:

$$U = \exp(S^1), \qquad (3.2.5a)$$

$$S^1 = Z\, sV \; ; \; b_I^1 \; e \; B_1 \qquad (3.2.5b)$$

and construct a second intermediate operator

$$H_2 = U_1^{-1} H_1 U_1 - i\, U_1^{-1} \dot{U}_1. \qquad (3.2.5c)$$

Note that since both H_1 and S^1 belong to the Lie algebra L , H contains operators belonging to L only, since the Hausdorff multi- commutator expansion to H_2 generates only those operators of L . In other words B_0 type operators do not appear in H as long as S^1 is defined by eq.(3.2.5b). The unknown parameters s^1 are determined by requiring

$$Q_1 H_2 P_1 = 0. \qquad (3.2.5d)$$

By this, all the operators belonging to B_1 are eliminated from H_2 and it is now restricted to the algebra $L_2 = L_1 - B_1$. The proof of the closure of L is analogous to the proof that L is a closed algebra. Proceeding in this fashion we define

$$U_k = \exp(S^k), \tag{3.2.6a}$$

$$S^k = \sum s_I^k b_I^k \; ; \; b_I^k \in B_k, \tag{3.2.6b}$$

$$H_{k+1} = U_k^{-1} H_k U_k - iU_k^{-1}\dot{U}_k \tag{3.2.6c}$$

and determine s from

$$Q_k H_{k+1} P_k = 0. \tag{3.2.6d}$$

Each H and S^k belong to a closed algebra L = L - B and thus H . does not contain any operators B which have been eliminated in the earlier steps.

Carrying this procedure up to n-valence systems we finally obtain

$$U = U_0 U_1 U_2 \ldots U_n, \tag{3.2.7a}$$

$$U_k = \exp(S^k), \tag{3.2.7b}$$

$$S^k = \sum s_I^k b_I^k \; ; \; b_I^k \in B_k, \tag{3.2.7c}$$

where the governing equation for the generators S^k of each U are given without any reference to later operators U_{k+1} etc.. These remain frozen in the calculation for the states with more particles. Note that this decoupling of the equations and the consequent freezing of the S^k matrix elements in later

calculations follows from the existence of the sequence of sub algebras L_0 to L_k. Since each S^k corresponds to k valence particles, we essentially recover the subsystem embedding condition.

The wave operator constructed via eq.(3.2.7) converts the hamiltonian into a block triangular form. While this is sufficient to obtain its eigenvalues, it is not convenient to calculate non-energetic properties or transition matrix elements. Since the H_k are similarity transformations of H, it is possible to calculate such quantities only by obtaining both the left and right eigenvectors of H.[15] While the right eigenvectors are confined to the P space, the left eigenvectors span the full Hilbert space. As a consequence, their calculation requires as much effort as the corresponding full CI. For such calculations it is desirable to construct H_k that are block diagonal i.e., it satisfies

$$P_k H_k Q_k = 0 \tag{3.2.8}$$

in addition to eq.(3.1.4). We now turn to the construction of a wave operator that satisfies such a requirement while retaining the sub-system embedding condition. As before we define

$$U_0 = \exp(S^0),$$

$$S^0 = \sum s_I^0 b_I^0 \quad ; \; b_I^0 \in B_0,$$

$$H_1 = U_0^{-1} H U_0 - i U_0^{-1} \dot{U}_0$$

and we require that eq.(3.2.4d) be satisfied to determine s^0. We next define

$$U_0' = \exp(\Sigma^0), \tag{3.2.9a}$$

$$\Sigma^0 = \sum \sigma_I^0 a_I^0 \quad ; \quad a_I^0 \in A_0, \tag{3.2.9b}$$

$$H_1' = U_0'^{-1} H_1 U_0' - iU_0^{-1\prime}\dot{U}_0' \tag{3.2.9c}$$

and determine CT° matrix elements from

$$P_0 H_1' Q_0 = 0. \tag{3.2.9d}$$

/ /

H belongs to the set of operators L = L - A . As before, it can be shown that L is closed under commutation **and hence forms a Lie algebra.**

In the second step we eliminate B and **A operators we define as before**

$$U_1 = \exp(S^1),$$

$$S^1 = \Sigma s_I^1 b_I^1 \quad ; \quad b_I^1 \in B_1,$$

$$H_2 = U_1^{-1} H_1 U_1 - iU_1^{-1}\dot{U}_1$$

and determine s coefficients by eq.(3.2.5d). We then postulate U_1' by

$$U_1' = \exp(\Sigma^1), \tag{3.2.10a}$$

$$\Sigma^1 = \sum \sigma_I^1 a_I^1 \quad ; \quad a_I^1 \in A_1, \tag{3.2.10b}$$

$$H_2' = U_1'^{-1} H_2 U_1' - iU_1^{-1\prime}\dot{U}_1' \tag{3.2.10c}$$

and determine σ^1 coefficients by requiring

$$P_1 H_2' Q_1 = 0. \tag{3.2.10d}$$

Again it can be shown that $H_2^{/}$ belongs to the closed algebra $L_2^{/} = L_2 - A$. This process can be continued until all the n-valence A and B type operators are eliminated from the final effective hamiltonian. The final wave operator has the form

$$U = U_0 U_0 U_1 U_1 U_2 U_2 \ldots U_n U_n . \qquad (3.2.11)$$

Note that for zero valence problem, this operator reduces to the form suggested by Arponen in his development of the extended coupled cluster method.[13] The final H_k is of block diagonal form. Hence its left and right eigenvectors are confined to the model space. These can be used along with the effective operators

$$\bar{O} = U^{-1} O U \qquad (3.2.12)$$

to evaluate expectation values and transition matrix elements.

Once the U is constructed and hence the various H are defined, the dynamics within the model space are obtained from eq.(2.2.2b). For k-particle subspace, this is given by

$$i\dot{\phi}^{(k)} = P_k H_k P_k \phi^{(k)} . \qquad (3.2.13)$$

3.3. CONCLUDING REMARKS

In this chapter we have set out to develop the wave operator based on the sub-algebraic structure present in the operator set acting on the Fock space. Essentially we have argued that each similarity transformation should restrict the hamiltonian to smaller subalgebra. As a consequence, the exponential similarity transformation generated by the elements of

the smaller subalgebra does not regenerate the operators already eliminated. This follows from the multi-commutator expansion of the exponential similarity transformation. We have specifically derived two forms of the wave operator. The first of them is essentially the wave operator defined by Mukhopadhyay et al..[14] The second one is a multi-determinental reference function generalization of the extended coupled cluster method developed by Arponen. However on an operational level our approach differs from Arponen's work. We require that the effective hamiltonian have no A and B type operators while Arponen advocates the use of a bivariational principle. As a consequence, the calculation of s and σ variables is coupled in his approach. In contrast, the calculation of s variables in our approach is decoupled from the calculation of σ variables.

Extensions of this approach to systems containing several groups of distinguishable particles is trivially made. The Fock space of such a super system is formed by taking the direct product of the Fock spaces of the subsystems

$$F^S = F^1 \otimes F^2 \otimes \ldots \tag{3.3.1}$$

Similarly the various model spaces are formed by taking the direct products of the individual subsystem model spaces

$$M^S_{n_1 n_2 \ldots} = \prod_\alpha M^\alpha_{n_\alpha}. \tag{3.3.2}$$

The operator space active on the larger Fock space can be decomposed along the same lines as discussed in the previous section. We discuss such a decomposition for a specific example

in the next chapter and study the performance of various levels of approximation with a view to understand the convergence properties of TDCCM.

A few comments on the computational aspects of the present approach are in order. The working equations of the MRTDCCM developed above are nonlinear. As such an exact calculation by this approach is prohibitively costlier than a straight forward linear basis set expansion calculations in the same single particle basis. The major attraction that the MRTDCCM holds is in the hierarchy of nonperturbative approximations that can be defined. In electron correlation theories for example, it is well known that a two-body approximation to the cluster operator provides highly accurate results.[3] However, very little computational evidence is available in the context of time-dependent studies. Noteworthy among them are the works of Sebastian[19] who used TDCCM approach to study electron transfer reactions at the electrode surfaces, Durga Prasad[20] and Guha and Mukherjee[21] who studied dynamics of coupled oscillators. While these studies demonstrated the potentiality of the TDCCM approach they are not adequate to draw definite conclusions regarding the utility of the approach. We undertake some preliminary studies in that direction in the next two chapters on the other classes of systems.

We note in passing that our approach is dependent upon the choice of the single particle basis that is used to construct the Fock space. We term this approach as the basis set representation of the time evolution operator. It is possible to construct the operator set directly in terms of the coordinates and the momentum operators of all the particles in the system.

For a one dimensional anharmonic oscillator the Lie algebra of the hamiltonian in such a representation is

$$L_o = \{ Q_{mn} = q^m p^n;\ 0 \le m, n \le \infty \}$$
$$= \{ A_{mn} = b^{+m} b^n;\ 0 \le m, n \le \infty \},$$

where b and b are the usual harmonic oscillator ladder operators.

$$b^+ = [\sqrt{mw}(q-q_o) + i\sqrt{(1/mw)}(p-p_o)]/\sqrt{2\hbar}, \qquad (3.3.3)$$

$$b = [\sqrt{mw}(q-q_o) - i\sqrt{(1/mw)}(p-p_o)]/\sqrt{2\hbar}. \qquad (3.3.4)$$

The time evolution operator can be constructed using this algebra and its multi-dimensional generalizations. Such a study has been carried out by Madhavi Sastry et al..[22] The evolution operator in terms of the harmonic oscillator ladder operators has the same form as the present version in that it is normally ordered with respect to the harmonic oscillator eigenfunctions. We term this approach as the boson representation of the evolution operator. Notwithstanding the similarities, the two approaches have several differences. The hamiltonian in the boson ladder operator form in general does not commute with the number operator, while the hamiltonian in the basis set representation commutes. As a consequence, the generators in the boson representation can go up to infinite boson creation, where as in the basis set representation N-particle excitation is the maximum possible. Irrespective of the truncations imposed, the boson representation incorporates contributions from all the infinite basis functions in the Hilbert space of harmonic oscillators due to exponential

ansatz. On the other hand, the truncations in the single particle basis set define the limit of basis set contributions in **the** present approach. However, it is possible to chose the single particle basis set to suit the problem at hand in the present approach, while in the boson representation the flexibility is limited to only three variables p_o, q_o and w, which serve to define the harmonic oscillator algebra.

It is also possible to develop a mixed representation in which some degrees of freedom are described in terms of the boson ladder operators while others are represented by an explicit basis. Again the time-dependant wave operator can be written in normally ordered form by analyzing the sub-algebraic structure. We would make use of this representation also to study the intramolecular vibrational energy relaxation (IVR) dynamics in the next chapter and compare its performance with that of a pure basis set representation.

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CHAPTER IV

A MULTI-REFERENCE TIME-DEPENDENT COUPLED CLUSTER STUDY OF INTRAMOLECULAR VIBRATIONAL RELAXATION PROCESS

4.1. INTRODUCTION

The previous chapter was concerned about the derivation of the MRTDCCM approach from the Lie-algebraic perspective. As we noted there, very few studies have been made to assess the validity of the approximations suggested by the TDCCM approach in terms of the subsystem amplitudes. In this chapter we study the validity of such approximations to Intramolecular vibrational energy relaxation (IVR) process.

Dynamics of a localized vibrational excitation in a molecule when collisional and radiative interaction with the environment are negligible can be defined as intramolecular vibrational relaxation.[1] It provides insight into many experimental studies of unimolecular reactions and spectroscopic observations. Classical and quantum mechanical perspectives of such dynamics have attracted the attention of several authors recently.[1-] Theories of IVR developed up to 1990 were reviewed by Uzer.[15]

During the overtone excitation, a large amount of energy is trapped in one mode. This initially excited mode relaxes into the remaining vibrational modes of the molecule. In the polyatomic molecules there is a possibility that the energy of this excited mode matches with many other states and so the oscillator strength of the overtone excitation is distributed among the many molecular eigenstates resulting in broad spectral bands.

In anharmonic oscillators the oscillator frequency is a function of level of vibrational excitation and generally decreases with increasing energy content of the oscillator. Irreversible IVR is a consequence of sequential overlapping

nonlinear resonances between the initially excited anharmonic mode and the rest of vibrational modes during the course of its time evolution. The scenario for such IVR is as follows. The active mode is initially in resonance with one bath mode and continuously exchanges energy with it with a Rabi frequency equal to the coupling between the two modes. During this period its vibrational frequency would also oscillate. When the energy content in the active mode is lowest in this exchange its frequency is highest and at this stage of its evolution were it to become resonant with a third mode, it can exchange energy with that also. As a consequence, its energy content would fall further and its frequency increases to a larger value. A crucial requirement for the irreversible IVR is that the secondary increment of the active mode frequency destroys resonance between the active mode and the first bath mode. A sequence of such nonlinear resonances would further increase the time period over which no recurrence would occur. In the quantum mechanical picture the scenario continues with the modification that the vibrational frequencies are replaced with zero order transition energies between successive levels of the various modes. A noteworthy feature of the scenario is that the resonant transfer of energy from the active mode to bath modes at each stage is generally a two body process.

The quantum dynamical study of IVR requires numerical solution of the time dependent Schroedinger equation (TDSE)

$$i\hbar\, d\psi/dt = H\psi. \qquad (4.1)$$

The brute-force method to solve TDSE is to expand the time dependent wave function as a linear superposition of the basis

vectors of an appropriate Hilbert space and integrating the corresponding hamiltonian matrix.[4,8,9] The computational resources required to solve such configuration interaction (CI) approach increase exponentially with the number of degrees of freedom in the system.

Recently significant progress has been made in handling large basis sets for such calculations.[4,5] Wyatt and co workers[4] published a series of papers on the studies of quantum dynamics of overtone relaxation in benzene considering various model benzene systems. They contract the ultra large direct product primitive spaces to smaller active spaces making use of either an artificial intelligence (AI) tree pruning algorithm or an iterative wave operator (WO) sorting algorithm. The exact dynamics within this active space are then determined using recursive residue generation method (RRGM). Through the usage of lanczos tridiagonalization algorithms the computation and storage of all the eigenvectors can be avoided. Marcus and co workers[5] employed a modified RRGM in which even the tridiagonalization procedure is suppressed so that the dynamics of huge systems can be handled. Even though these AI and WO algorithms reduce the dimension of the basis set to be handled, that reduced dimension itself is in the order of a few thousands, which require quite high computational resources.

Makri et al.[6] developed a procedure based on path integral formulation for the propagator when the coupling between the active (initially excited) mode and the bath modes is linear in the bath coordinates and bath modes are subject to harmonic potentials.

Alternative methods which are useful in the description

of IVR are dynamical basis set methods based either on the semiclassical gaussian wave packet propagation (GWP) technique[16-19] or the time dependent self consistent field (TDSCF) approximation.[20] In the GWP method the wave packet is expanded in terms of travelling gaussians[18] as described in Chapter I. The TDSE is propagated by integrating each gaussian independently. The resulting equations for position and momentum are classical Hamilton's equations. This gives a convenient picture to describe the process in terms of classical trajectories. To the best of our knowledge this method has not been used so far to describe the IVR process. In TDSCF method each mode in the system is formally separated and is governed by time-dependent average potential obtained by averaging the full potential over all other degrees of freedom. As each mode is treated individually in this approach the correlations among the modes are not accounted for. So in this approach the irreversible energy decay and the resonant energy transfer can not be described properly as these phenomena involve resonant interaction of two or more modes. To explain these phenomena, a many body treatment is necessary. The TDSCF has recently been extended to include such higher body effects wherein the required configurations are added. These MCTDSCF[24] versions also face the problem of exponential growth of basis for the configuration interaction part.

The MRTDCCM[25] accounts for the higher body correlations in terms of corresponding cluster operators and is expected to provide a good description of the IVR dynamics. In this approach a group of strongly interacting states are identified as model space. The full time evolution operator is split into two parts. The first part describes the evolution of

the projection of wave packet in the model space. The second part which is analogous to the Moller wave operator in the stationary state theories,[29] maps the model space component to the full wave function. An exponential ansatz is posited for the time-dependent wave operator. The dynamics within the model space are treated exactly and the approximations are confined to the construction of wave operator which accounts for the weaker interaction between the model space and the virtual space. As a consequence of the exponential form, the generators of the wave operator are additively separable. This allows one to decompose the dynamics in terms of subsystem dynamics. To this end we study two model systems using the **MRTDCCM** formalism.

In **sec.4.2** we present the details of our first system, a model hydrocarbon chain, construction of the evolution operator, and dynamics and convergence properties using two representations: One is the basis set representation and the other mixed representation (discussed in Chapter III). In **sec.4.3** we study another system which is derived by simply considering the first system in a radiation field of particular field strength. In the last section **(sec.4.4)** we present the conclusions we have drawn on the applicability of MRTDCCM approach for determining the **IVR** dynamics.

4.2. **IVR** DYNAMICS IN A MODEL HYDROCARBON CHAIN

4.2.1. The System :

In this section we introduce our first system and review its features. We study IVR dynamics in a simple hydrocarbon chain

model developed earlier by Hutchinson et al.[8-15] that consists of 11 carbon atoms with a hydrogen atom attached to one of the terminal carbons. The CC bonds are taken to be harmonic and the CH oscillator is taken to be a Morse oscillator. The initial conditions are defined such that the CH oscillator is in one of its excited eigenstates at t = 0. Hutchinson et al. found that only four of the highest frequency normal modes of the CC chain receive energy in the dynamical flow due to nonlinear resonances present in the system.[8,] So, only these four modes (M) are retained. In terms of these coordinates q_i and momentum p the hamiltonian is given by

$$H = H_o + V , \qquad (4.2.1a)$$

$$H_o = p_{CH}^2 /2\, \mu_{CH} + D\,(1 - \exp(-\alpha\, q_{CH}))^2 + 1/2 \sum_{i=1}^{4} (p_i^2 + \Omega_i^2\, q_i^2), \qquad (4.2.1b)$$

$$V = - 1/m_C \sum_{i=1}^{4} L_{11}^{-1}\, p_{CH}\, p_i , \qquad (4.2.1c)$$

where i is the harmonic mode index. D and a are the Morse parameters for the CH bond. D = 3.647 eV and α = 1.0688 a^{-1} and μ is the reduced mass of CH oscillator. The remaining parameters were taken from ref. 8 and are collected in Tab.4.1.

Table 4.1 Oscillator parameters **for C H**

Mode	Ω_i (cm^{-1})	L_{11}^{-1} (amu^{-1})
M_1	2200	-0.80
M_2	2380	0.61
M_3	2509	0.42
M_4	2590	0.21
CH bond	2950	

We next specify the basis set. The eigen functions of H_0 are the oscillator product states $|m\rangle|n_1\rangle|n_2\rangle\backslash n_3\rangle|n_4\rangle$, where m is the quantum number of the Morse oscillator and n is the quantum number of the i th harmonic oscillator. We have studied dynamics **for** two initial conditions, with quantum numbers m = 4 and 5 at t=0. We have taken M = max(m) = 4 and 5, for these two initial conditions. Hutchinson et al.[8] found that each chain **mode** receives only a small amount of energy, so we take N • $\max(n_i)$ = 1 for each normal mode harmonic oscillator. The resultant basis sets are N =80 for the dynamics of |4,0,0,0,0> state and N_t = 96 for the |5,0,0,0,0> state.

The **MRTDCCM** is a Fock space theory. It is thus convenient to rewrite the **hamiltonian** in the second quantized form in terms of the single particle basis functions used to construct the hamiltonian. This gives

$$H_0 = \sum_{\alpha, n_\alpha} \varepsilon^{\alpha}_{n_\alpha} a^{\alpha^+}_{n_\alpha} a^{\alpha}_{n_\alpha} , \qquad \textbf{(4.2.1d)}$$

$$V = \sum_{\substack{\alpha,\beta,m_\alpha \\ m_\beta,n_\alpha,n_\beta}} \langle \alpha\, m_\alpha \beta\, m_\beta | v | \alpha\, n_\alpha \beta\, n_\beta \rangle\, a^{\alpha^+}_{m_\alpha} a^{\beta^+}_{m_\beta} a^{\alpha}_{n_\alpha} a^{\beta}_{n_\beta} . \qquad (4.2.1e)$$

Here a, β denote vibrational mode and m, n denote the basis functions of these modes. a^{α^+} ($a^{\alpha}_{\sim}$) are the usual creation and annihilation operators associated with these functions. Fig.4.1a depicts the terms diagrammatically.

Two features of the hamiltonian are worth noting. First, since the perturbation term V contains only momentum coupling operators, the TDSCF would predict only trivial dynamics for this system in which only the phase of the wave function would change in time. Second, as noted by Hutchinson et al., several near degeneracies exist among the zeroth order states of the system due to the CH bond anharmonicity. For example, the |5,0,0,0,0> is nearly degenerate with |4,l,0,0,0> and |4,0,l,0,0> states. These states are coupled to the initial state by two body operators. Hutchinson et al. have shown that these near degenerate states can be put into different tiers and only states in the neighbouring tiers (which differ in the occupation numbers of two modes) are coupled by the perturbation (eq.(4.2.1c)). Thus an approximation to the time evolution operator containing only two body operators should provide a good description.

4.2.2. The MRTDCCM ansatz

We now turn to the parametrization of the time dependent wave function in the MRTDCCM frame work. In this approach, the wave packet ϕ at t = 0 is taken to be an element of a small

subset of strongly interacting states { ϕ_ν^o } of the full Hilbert space. This subspace is called as model space. This state evolves in time under the influence of the time evolution operator U that satisfies the TDSE

$$\psi = U_F \phi_o , \tag{4.2.2a}$$

$$i \dot{U}_F = H U_F . \tag{4.2.2b}$$

Within the frame work of the time dependent effective hamiltonian theory,[28,30] as described in Chapter II, U is partitioned as

$$U_F = U U_M , \tag{4.2.3}$$

where U_M is the model space evolution operator that describes the dynamics of component of the wave function in the model space and U brings out admixture of model space and the virtual space.

The time dependent coupled cluster method[28] posits an exponential ansatz for the time dependent analog of the Moller wave operator[29] that maps the model space projection $<p$ onto the full wave function ψ

$$\psi = U \phi, \tag{4.2.4a}$$

$$U = \exp(S). \tag{4.2.4b}$$

Here S is an operator that induces transitions from the model space to the virtual space. We note in passing that our ansatz

(4.2.4b) for U is somewhat different from the choice of Guha and Mukherjee[28], who prefer a normally ordered exponential ansatz

$$U = N [\exp(S)]. \qquad (4.2.5)$$

The number of terms in the working equations are fewer if a normally ordered ansatz is used for U.

4.2.3. The Model space definition and the evolution operator:

4.2.3a. Basis set representation:

We begin our analysis by classifying single particle states as envisaged in Chapter III. As an illustrative example to motivate the choice of our model space we have considered the evolution of initially prepared |5,0,0,0,0>. Hutchinson et al. found that this state is in near resonance with |4,1,0,0,0> and |4,0,1,0,0> states. |4,0,l,0,0> state in turn interacts strongly with |3,0,l,l,0> state and so on. A common feature of all these states is that the Morse oscillator quantum number changes in all of them. Thus we classify all the Morse oscillator states as valence states, the ground states of all the harmonic oscillators as hole states and excited states as particle states. Thus our model space consists of all the states { |m,0,0,0,0>;0≤ m≤ M). Although these states do not interact strongly we were motivated to choose this model space because, first this model space provides a one to one correspondence with the Morse oscillator states. Thus it can be used to construct an effective hamiltonian for the active mode alone. Second, all the states that are

degenerate with the intial state can be reached via the action of two body operators on the model space. For example, the $|4,1,0,0,0\rangle$ state can be reached by the action of the operator $a_4^{1+} a_5^1 a_1^{2+} a_0^2$ on $|5,0,0,0,0\rangle$. (Here the superscripts indicate the mode number, where 1 is the Morse mode and 2 to 5 are harmonic modes. The subscripts indicate the state number). This provides a natural cut off for making approximations to the cluster operators at the two body operator level. Third this choice provides a stringent test for the effective hamiltonian theory when the wave packet makes significant excursions outside the model space.

Following the analysis of operator manifold present in the Chapter III we now classify the operator set for the system:

$$C_0 = \{ 1 \}$$

$$C_1 = \{ a_m^{1+} a_n^1; \quad 0 \le m,n \le M \}$$

$$B_0 = \{ a_{v_i}^{1+} a_0^1, \; a_{v_i}^{1+} a_0^1 a_{v_j}^{j+} a_0^j, \ldots; \quad 0 \le v_i, v_j \le N_i, \; 2 \le i,j \le 5 \}$$

$$B_1 = \{ a_m^{1+} a_n^1 a_{v_i}^{i+} a_0^i, \; \ldots; \quad 0 \le v_i \le N_i, \; 2 \le i \le 5, \; 0 \le m,n \le M \}.$$

The closed operators belonging to C and C contribute to the model space effective hamiltonian H_M and thus to U_M. The open from below operators B and B contribute to the cluster operator that generates U. Following eg.(3.2.7) U can now be written as

$$U = U_0 U_1, \qquad (4.2.6a)$$

$$U_0 = \exp(S^0); \quad S^0 \in B_0, \tag{4.2.6b}$$

$$U_1 = \exp(S^1); \quad S^1 \in B_1. \tag{4.2.6c}$$

The governing equations for S are decoupled from those of S due to subsystem **embedding** condition. These equations are given by

$$(U_0^{-1}HU_0 - iU_0^{-1}\dot{U}_0)_{B_0} = 0. \tag{4.2.6d}$$

It can be verified by direct substitution that $U_0^{-1}HU_0$ does not have any B type operators. Consequently $U_0 = 0$ and $U_0 = 1$ for all times. Thus

$$U = U. \tag{4.2.6d}$$

With our choice of the model space and the operator set, the cluster operator S^1 consists of operators that excite the bath modes and simultaneously cause scatterings **among** the Morse states:

$$S^1 = S_2^1 + S_3^1 + \ldots, \tag{4.2.7a}$$

where

$$S_2^1 = \sum_{i,p_i} \langle m\ p_i\ |S_2|\ n\ h_i \rangle\ a_m^{1+}\ a_{p_i}^{1+}\ a_n^1\ a_{h_i}^1, \tag{4.2.7b}$$

etc.. Some of these are depicted **diagrammatically** in **Fig.4.1b.** Derivation of the working equations for the cluster matrix elements (eq.(4.2.7)) is conveniently carried out in diagrammatic notation. The **diagrammatic** equation for $i\dot{S}^1$ is presented in Fig. 4.2a and $i\dot{S}_3^1$ in **Fig.4.2b.** The equation for H is **presented in**

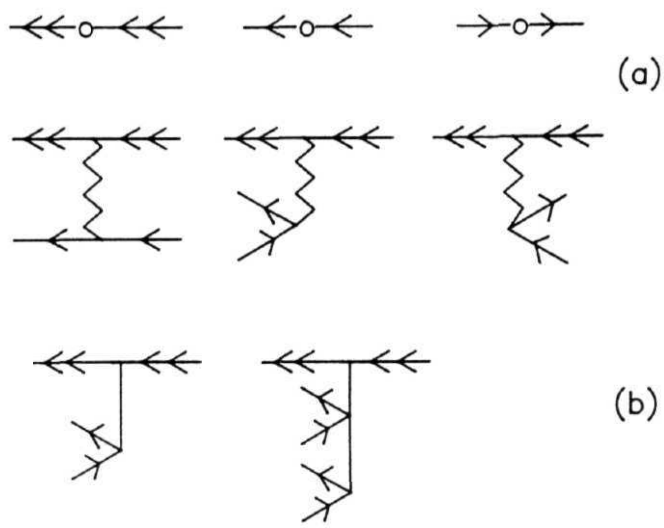

Fig. 4.1 Diagrammatic representation of (a) the hamiltonian of system-I, (b) S_2^1 and S_3^1 operators in basis set representation. Double arrows represent the Morse states of the CH oscillator and the single arrows represent the particle and hole lines of the harmonic bath modes.

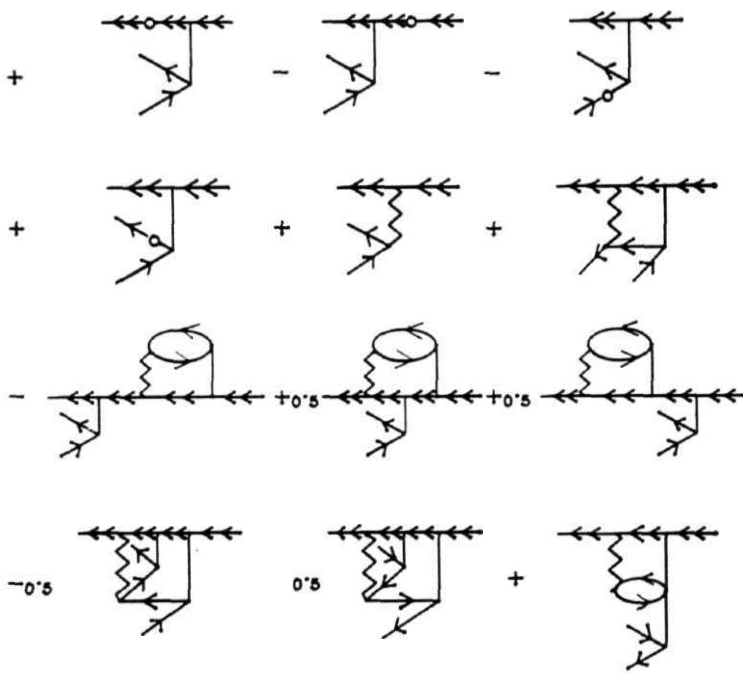

Fig.4.2a The diagrammatic representation of the equations of is in the basis set representation of **system-I.** The notations **are** the same as in Fig. 4.1.

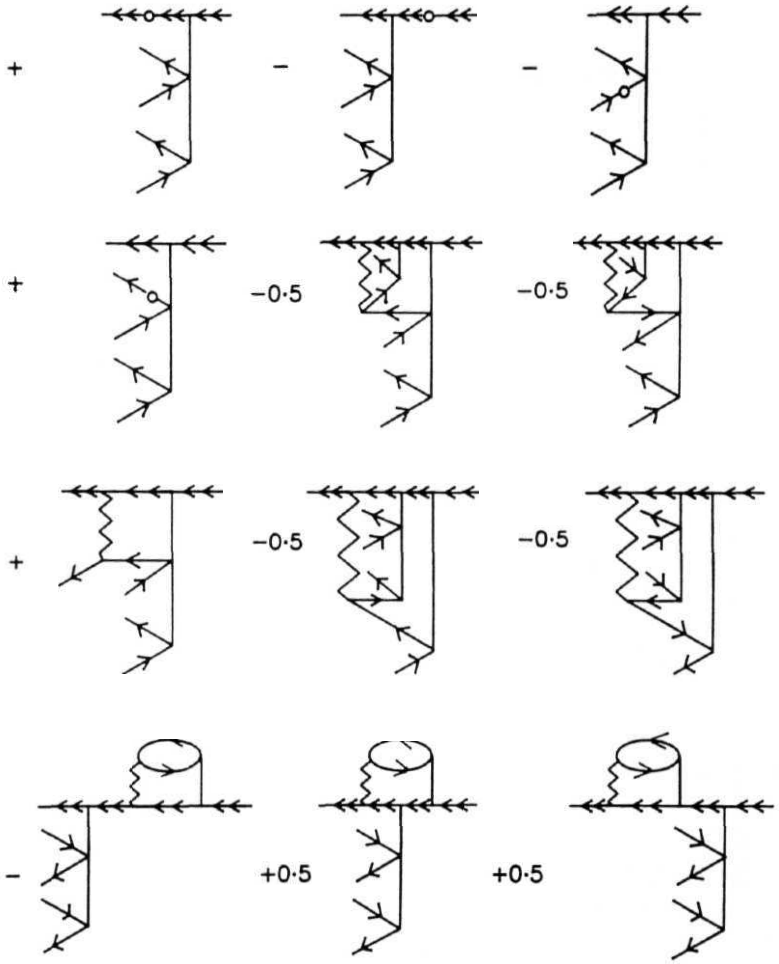

Fig. 4.2b Continued

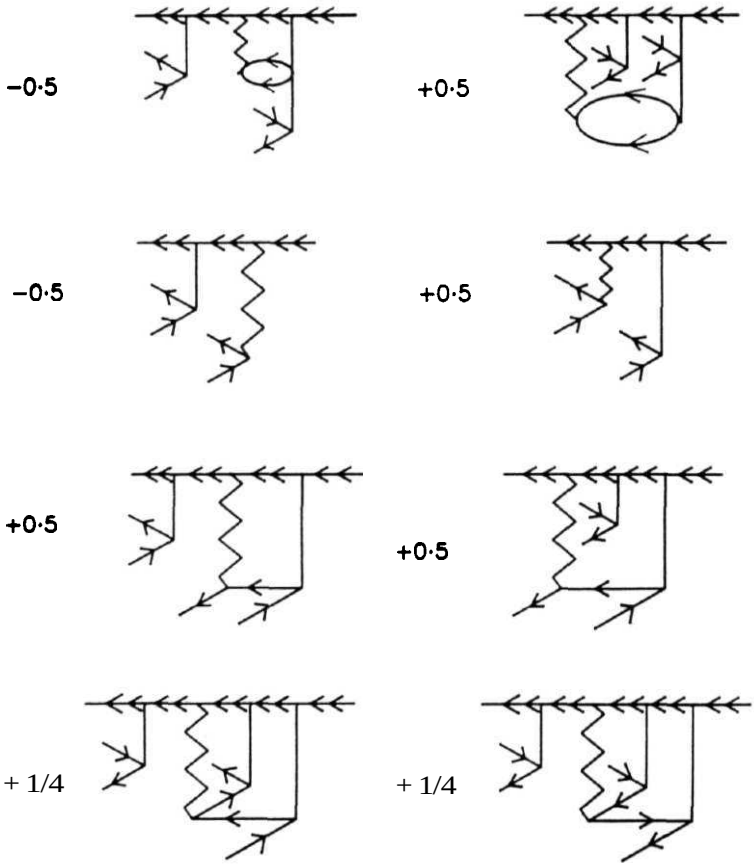

Fig. 4.2b Continued

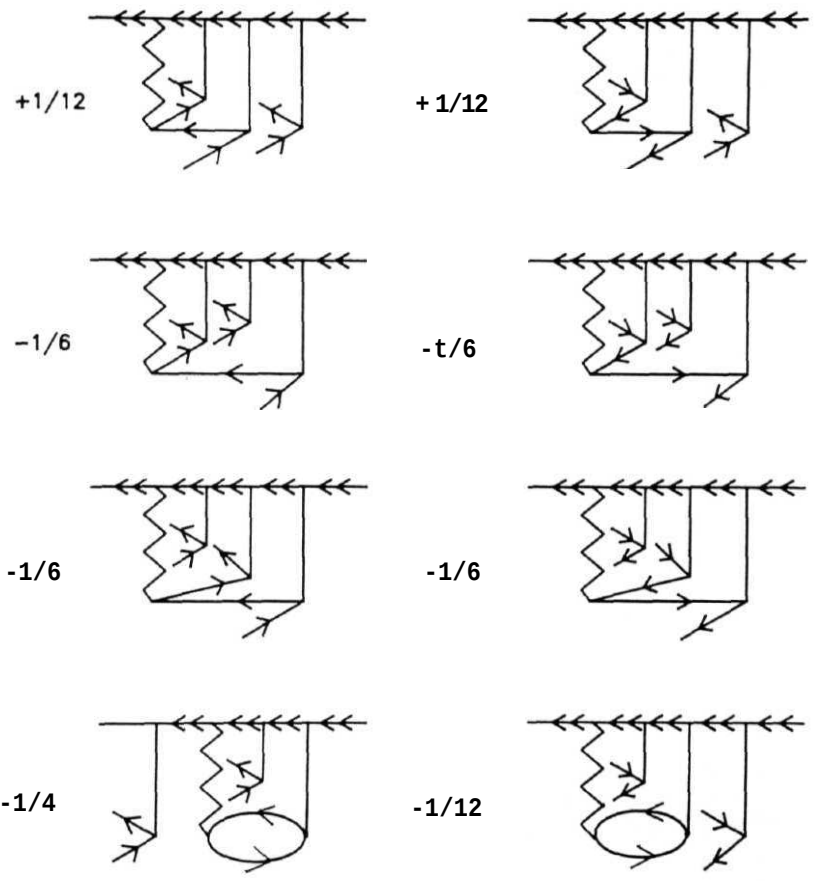

Fig. 4.2b Continued

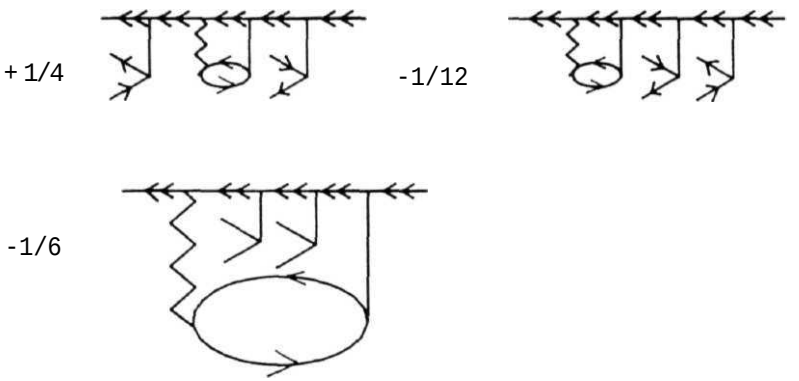

Fig.4.2b The diagrammatic representation of the equations of is^1 in the basis set representation of system-I. The notations are the same as in Fig. 4.1.

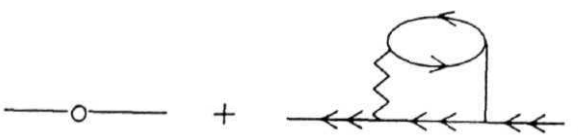

Fig. 4.2c The diagrammatic representation of H of system-I in basis set representation.

Fig.4.2c where

$$\bar{H} = P_1(U_1^{-1}HU_1 - iU_1^{-1}\dot{U}_1)P_1. \qquad (4.2.7c)$$

The model space component of the wave function $\phi = P\psi$ is determined from the equation

$$i\dot{\phi} = \bar{H}\phi, \qquad (4.2.7d)$$

$$\phi = \sum_k C_k(t)\phi_k;\ \phi_k \in M. \qquad (4.2.7e)$$

We solve the differential equations for ϕ and s^1 and s^1 using fourth order Runge-Kutta scheme. The survival probability of the initial state is calculated as $|C_M|$ where M is the quantum number of the Morse vibrational state to which it is initially excited. The expectation values of the energy in each mode are calculated by constructing the total wave function.

4.2.3b. Mixed representation:

In this representation we treat all the bath harmonic oscillators in terms of boson ladder operators and the Morse oscillator in the basis set representation. The **hamiltonian** in this representation is written as

$$H_0 = \sum_m \epsilon^1 a_m^{1+} a_m^1 + \sum_\alpha \Omega_\alpha (b^{\alpha+} b^\alpha + 1/2), \qquad (4.2.8a)$$

$$V = \sum_\alpha L_{1\alpha}^{-1} \langle m|p|n\rangle\, a_m^{1+} a_n^1 (b^\alpha - b^{\alpha+})/\sqrt{2}, \qquad (4.2.8b)$$

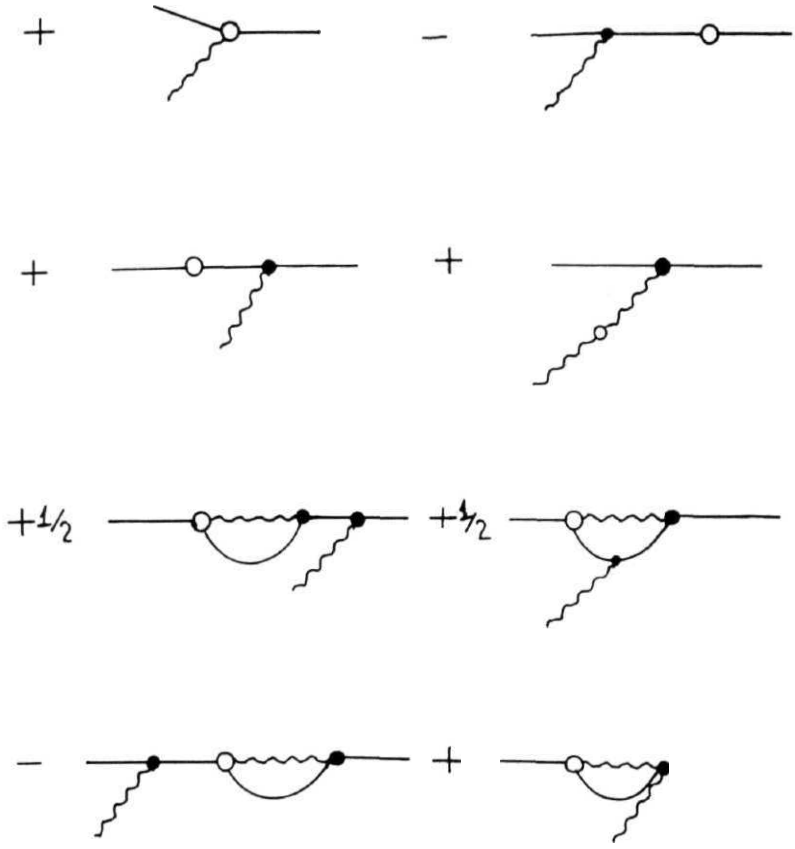

Fig. 4.3a

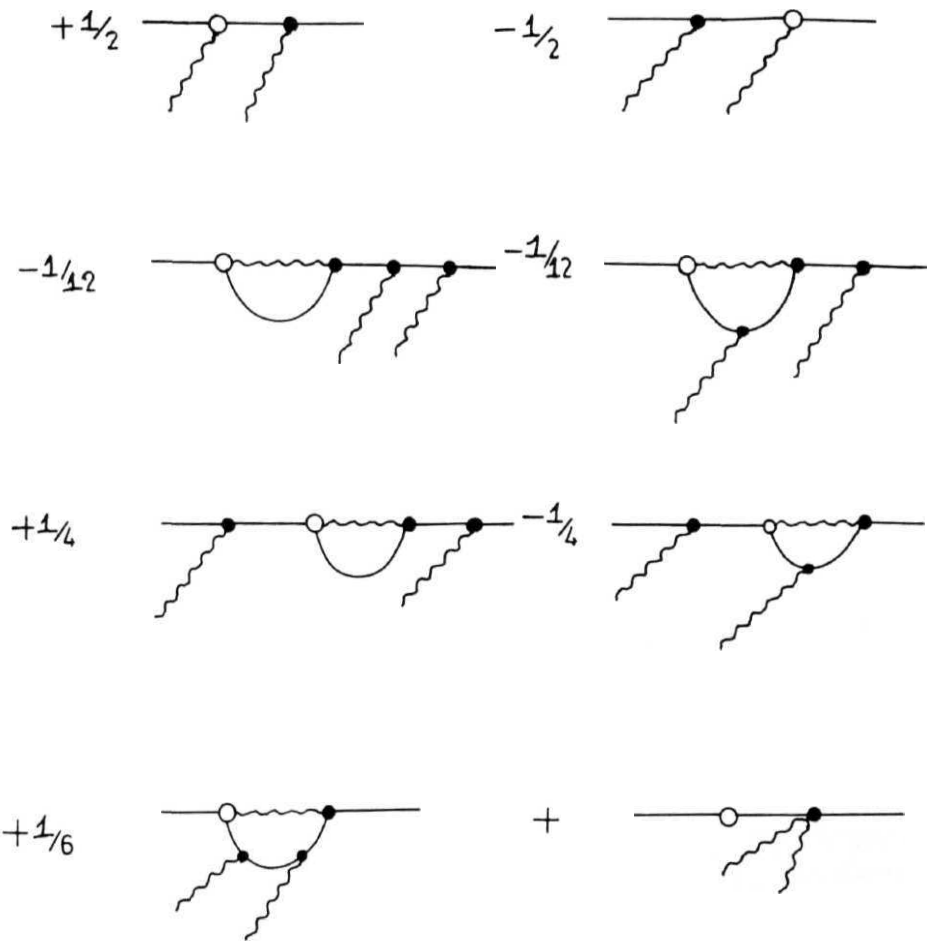

Fig. 4.3b Continued

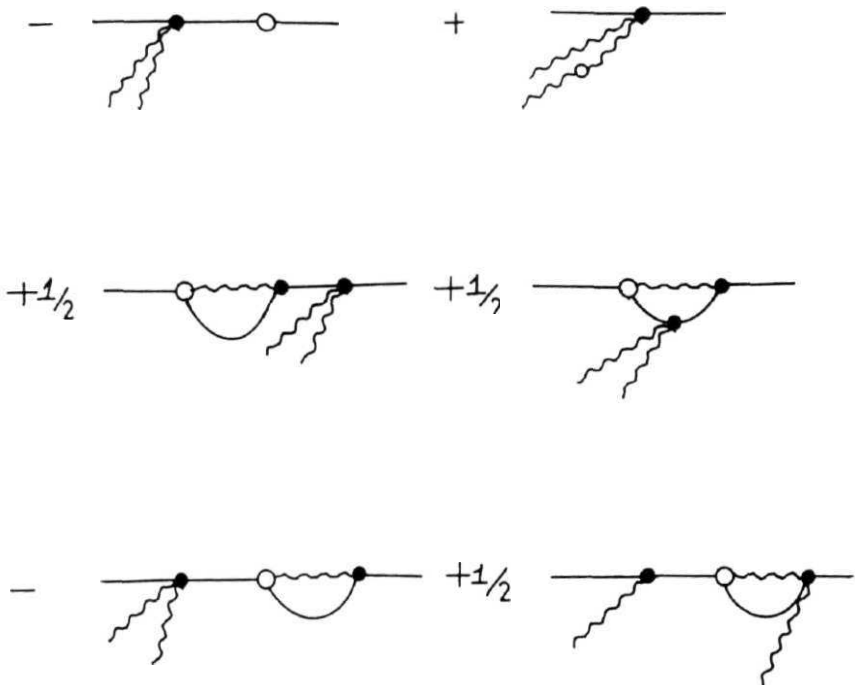

Fig.4.3 The diagrammatic representation of the equations (a) is **and** (b) is[1] in **the** mixed representation of **system-I.** The circle represents the **hamiltonian** vertex and dot represents **the** cluster operator vertex. Wiggly line represents a bosonic propagator and the straight line represents the morse propagator. Since **all the** lines move to the left no arrows have been used.

where α is the bath mode. We continue to use the same model space as in the previous study. The operator analysis holds here also, and only U_1 is required for obtaining the dynamics. The cluster operator S^1 of eq.(4.2.6c) in this representation is

$$S^1 = S_1^1 + S_2^1 + \ldots \qquad \textbf{(4.2.8c)}$$

where

$$S_1^1 = \sum_{m,n} S_{mn\alpha}^1 \, a_m^{1+} a_n^1 \, b_\alpha^+ , \qquad (4.2.8d)$$

etc. Here m, n are the Morse oscillator basis functions. The governing equations for $\dot{S}_1^1$ and $\dot{S}^1$ are presented in the diagrammatic notation in Fig.4.3. The survival probability of the initial state is calculated in a similar manner as in the basis set representation.

4.2.4. Dynamics and Convergence:

We first present the results of the dynamical calculations for survival probability of the initial state in the basis set representation. The survival probability when the initial wave packet is |4,0,0,0,0> is presented in Fig.4.4. The MRTDCCM calculations were carried out at $S^1 = S^1$ and $S^1 = S^1 + S^1$ approximations. We have also carried out a MRTDCCM calculation with normally ordered exponential wave operator[28] at $S^1 = S^1$ level for comparison. The working equations for this calculation are obtained by dropping the S-S contraction terms in the ordinary exp(S) theory. As can be seen from Fig.4.4 the MRTDCCM at $S^1 = S^1$ level provides a very good description of the irreversible decay

of the initial state, and the inclusion of the three body operator improves the result. In contrast, the normally ordered ansatz shows artificial recurrences as early as 4 vibrational periods. As is well known, the usage of normally ordered exp(S) ansatz with the two body approximation is equivalent to carrying out the dynamical calculations in a limited basis consisting the model space and all the singly excited states generated from it for the one valence problem.[32] This limited basis set is the origin of these recurrences. In the ordinary exp(S) theory on the other hand 2, 3 and 4 body excitations also influence the dynamics due to S-S contractions, though the coefficients of such configurations are parametrized as products of the lower rank excitation operators.

Survival probability corresponding to the initial state |5,0,0,0,0> is presented in Fig.4.5 . The trends in this case are similar to those in Fig.4.4. However, after about 5 vibrational periods the survival probability starts increasing when ordinary exp(S) ansatz is used. We traced this artificial rise to the violation of norm in the MRTDCCM approach. The MRTDCCM uses a similarity transformation to map the model space component of the wave function to the exact wave function. As noted in the ref. 30 and in Chapter II, the similarity transformation based methods are prone to norm violations due to intruder states that develop complex eigenvalues when the approximations invoked violate the hermiticity of the hamiltonian.

The energy in the Morse oscillator with the initial state |4,0,0,0,0> is plotted in Fig. 4.6. As may be seen the trends are similar to Fig. 4.4 in that the ordinary exp(S) theory performs better than the normally ordered exp(S) theory and the inclusion

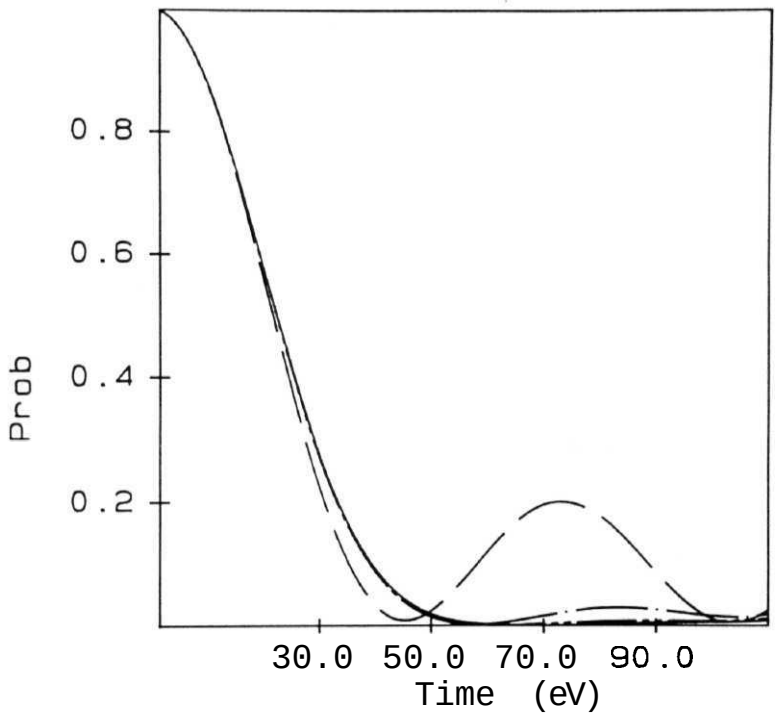

Fig. 4.4 The survival probability of the initial state |4,0,0,0,0> in system-I in the basis set representation. Continuous line: the basis set exact results. Dashed line: normally ordered MRTDCCM calculation at S^1 level. Dash and dotted line: Ordinary MRTDCCM at S_2^1 level. Dash and double dotted line: MRTDCCM at S^1 level of approximation.

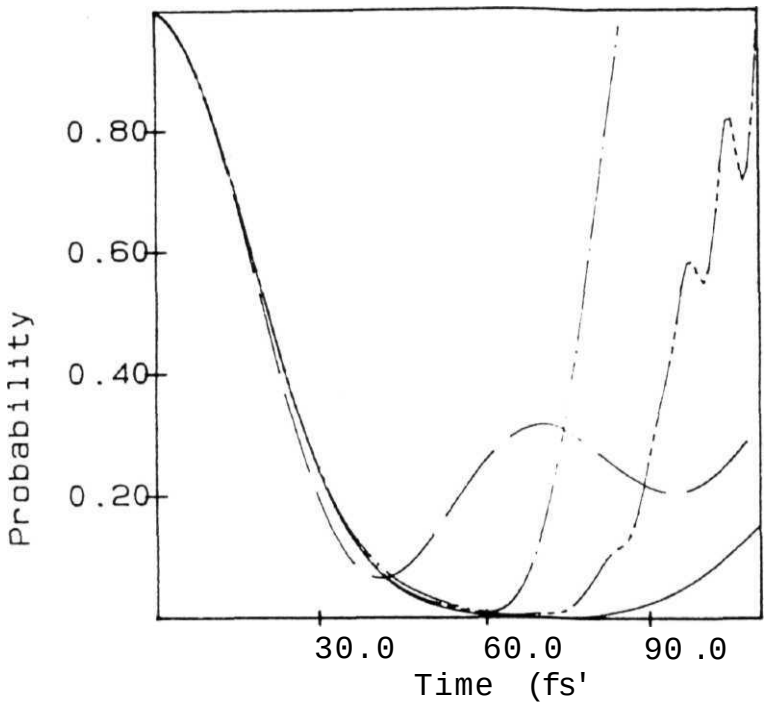

Fig. 4.5 The survival probability of initial state |5,0,0,0,0> in system-I in the basis set representation. The figure conventions are the same as in Fig.4.4.

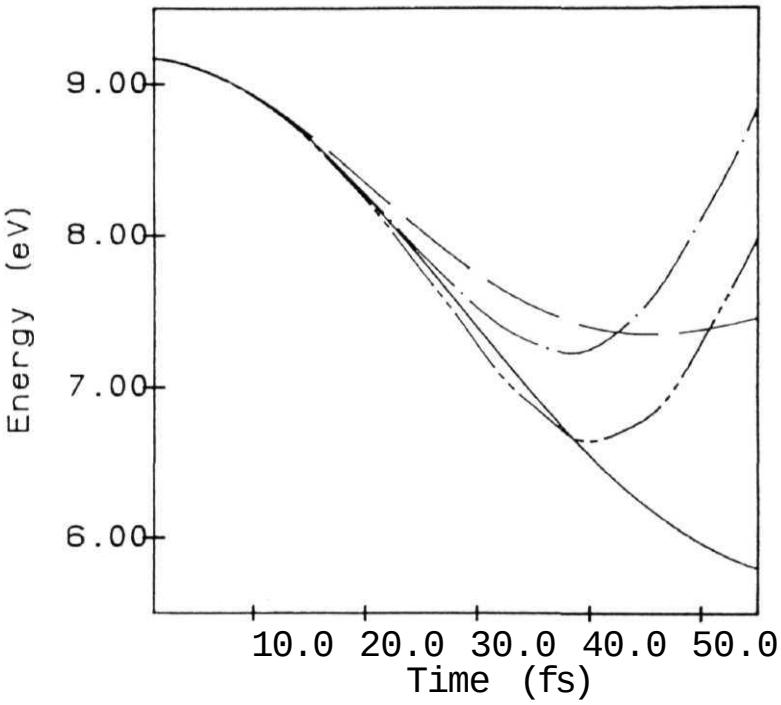

Fig. 4.6 The energy of the CH mode when ' the initial state is |4,0,0,0,0> in system-I in the basis set representation. The figure conventions are the same as in Fig. 4.4.

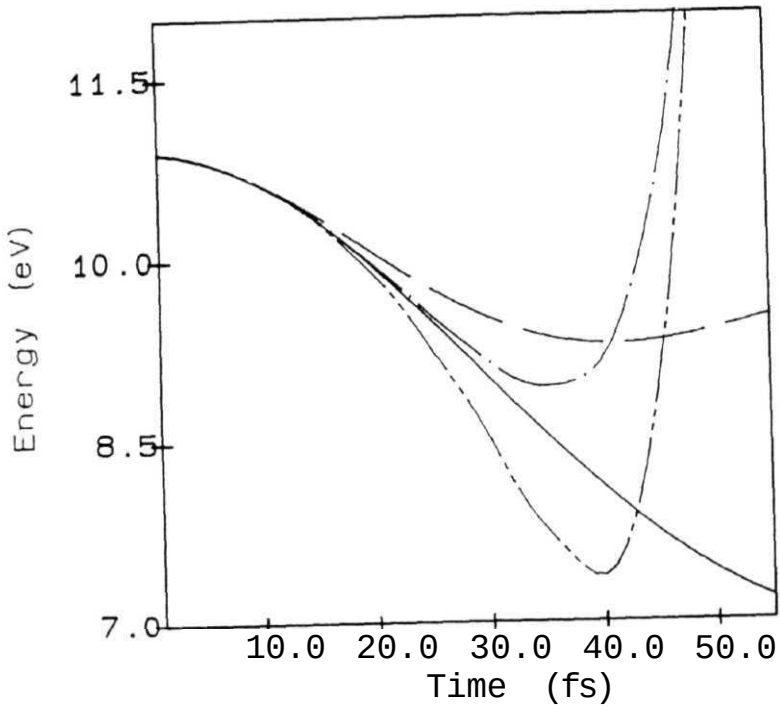

Fig. 4.7 The energy of the Morse mode when the initial state is |5,0,0,0,0> in system-I in the basis set representation. The figure conventions are the same as in Fig.4.4.

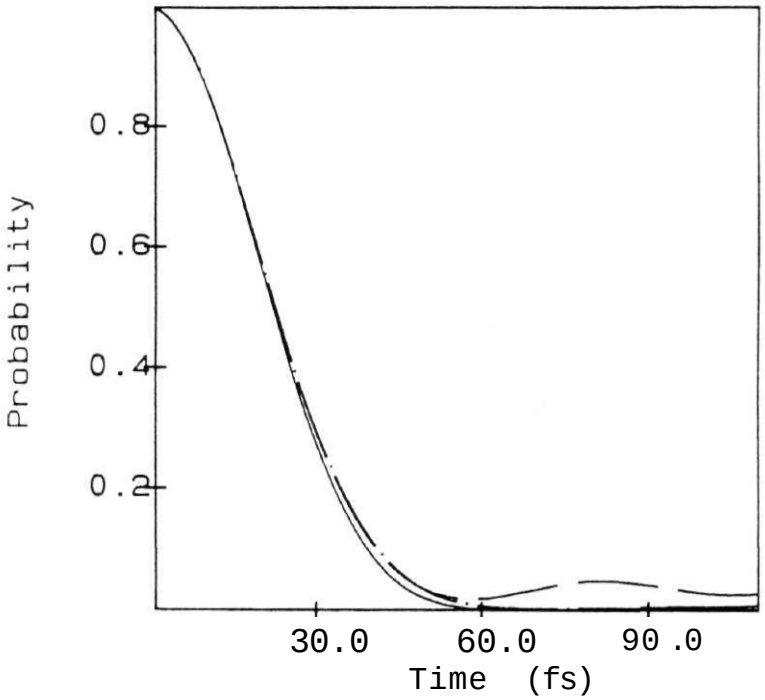

Fig. 4.8 The survival probability of the initial state |4,0,0,0,0> in system-I in the mixed representation. Continuous line: Exact calculation. Dashed line: ordinary MRTDCCM at the S^1 level. Dash and dotted line: S^1 level.

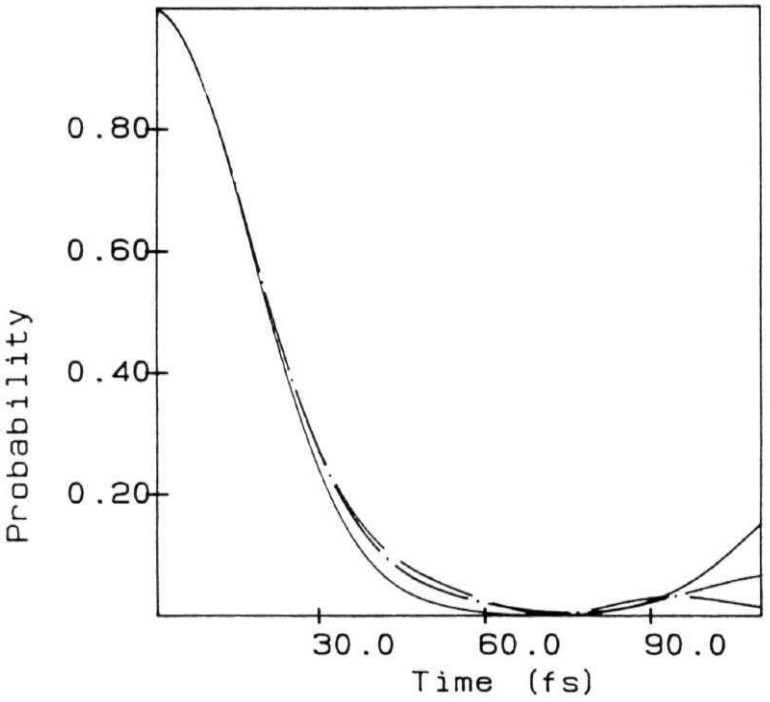

Fig.4.9 The survival probability of the initial state |5,0,0,0,0> in **system-I** in the mixed representation. The figure conventions are the same as in Fig. 4.8.

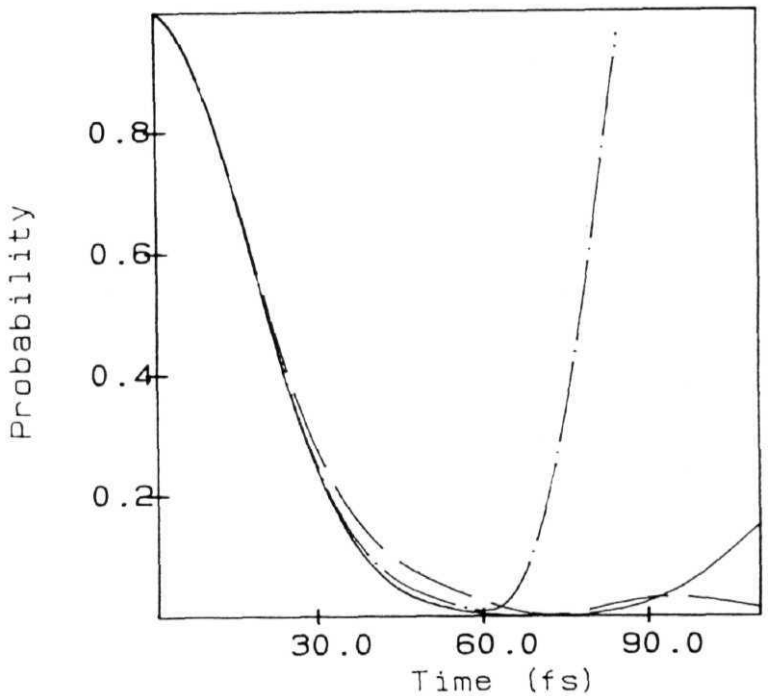

Fig.4.10 The survival probability of the initial state |5,0,0,0,0> in system-I. Continuous line: Exact calculation. Dashed line: MRTDCCM at S level in the mixed representation. Dash and Dotted line: MRTDCCM calculation at S^1 level in the basis set representation.

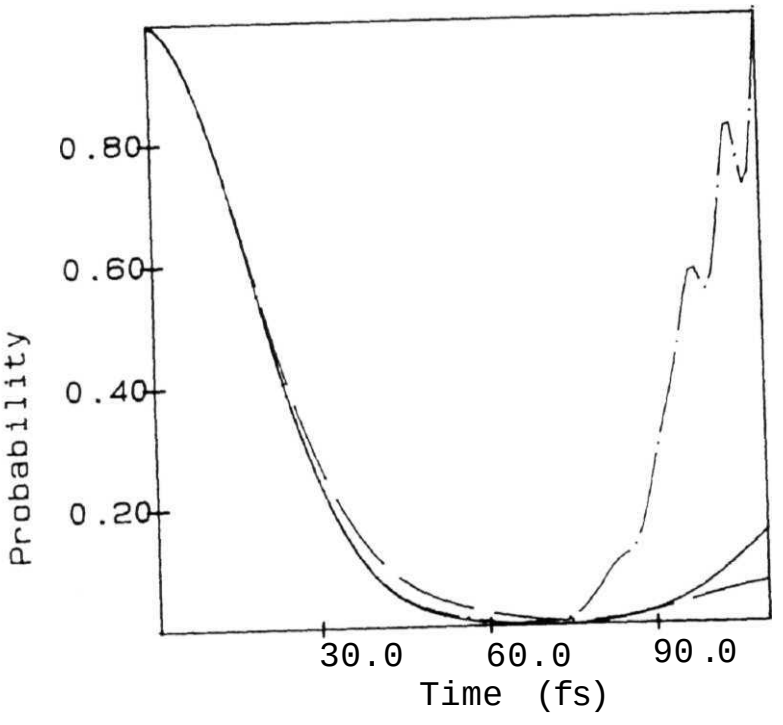

Fig.4.11 The survival probability of the initial state |5,0,0,0,0> in system-I. Continuous line: **Exact calculation.** Dashed line: S^1 approximation in mixed representation. Dash **and** dotted line: S approximation in the basis set representation.

of the three body operator improves the agreement with the exact result in the correct direction, extending the range over which the ordinary MRTDCCM is accurate. However, after about four vibrational periods the energy content in the Morse oscillator starts increasing, again due to norm violations. Similar trends are also seen in the energy of the Morse oscillator when the initial state is |5,0,0,0,0> (Fig. 4.7).

The survival probability when the initial wave packet is |4,0,0,0,0> calculated using mixed representation of MRTDCCM formalism is presented in Fig.4.8. These calculations are carried out at $S^1 = S_1^1$ and $S^1 = S_1^1 + S^1$ approximations and are compared against exact calculation. The result of S^1 approximation itself is in very good agreement with the exact calculation and with the inclusion of S_2^1 operators the result is exactly coincident with the exact calculation within the drawing accuracy. The survival probability when the initial state is |5,0,0,0,0> presented in Fig.4.9. Again S^1 approximation is quite good and the S^1 approximation, while not exactly coincident with the exact calculation, is very close to it.

A comparative study of the convergence of the basis set representation and the mixed representation are made in the Figs.4.10 and 4.11. Fig.4.10 compares the plots of survival probability when the initial state is |5,0,0,0,0> of exact calculation, S_2^1 approximation of the basis set representation and S^1 approximation of the mixed representation. After 60 fs S^1 approximation of basis set representation calculation blows up due to the norm violation effects, whereas the S^1 approximation of the boson representation is closer to the exact calculation for a much longer time. Similar trends are seen in the Fig.4.11, which

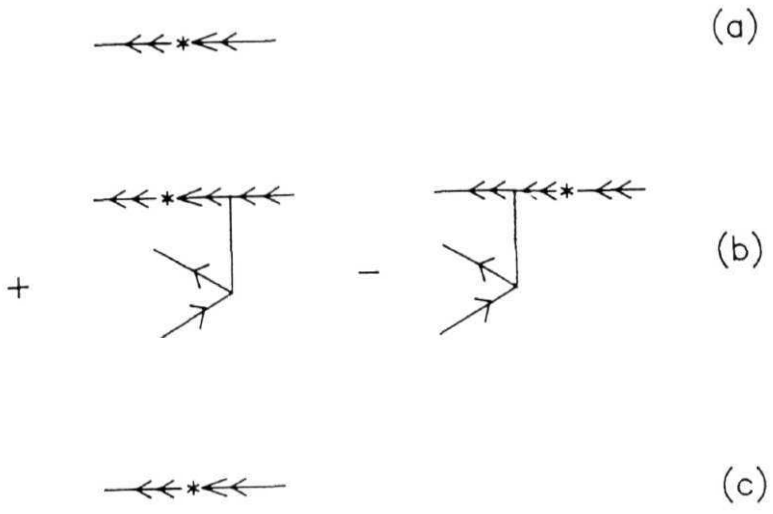

Fig.4.12 The additional diagrams that come for system-II. (a) Hamiltonian part and (b) the extra terms that add to is^1 equation in Fig.4.2a. (c) the extra H diagram that add to Fig.4.2c. The notations are the same as in Fig.4.1.

compares the calculations of exact, S^1 approximation in the basis set representation and S^1 approximation in the mixed representation.

4.3. IVR DYNAMICS IN MODEL SYSTEM-II

4.3.1. The System :

This model system is obtained by assuming that C-H oscillator of system-I is driven by an external radiation field. The hamiltonian of this system consists of one additional term V to the hamiltonian of the first system H.

$$V = A\, q_{CH} \cos(w\, t_r), \qquad (4.3.1)$$

where A is the field strength and w is the frequency of the radiation field. Fig4.12a depicts V diagrammatically. In our calculations we have set equal w such that the initial state $|0,0,0,0,0\rangle$ is in 4:4 resonance with the final state $|4,0,0,0,0\rangle$. The calculations are carried out in the basis set representation and the cluster expansion is truncated after S_2 approximation. The additional diagrams that come for iS_2 for this system are shown in Fig.4.12b and additional H diagram in Fig.4.12c.

4.3.2. Dynamics and Convergence:

We have computed the survival probability of the initial state, the probability in the final state and the energy of the Morse mode using MRTDCCM at $S = S_2^1$ approximation. In Fig.4.13 we have plotted the survival probability of the initial state as a

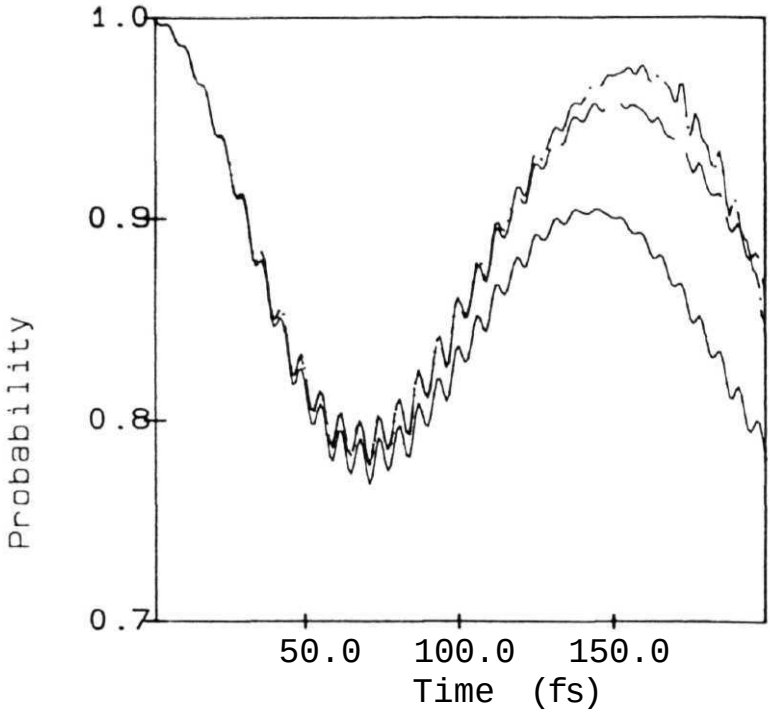

Fig.4.13 The survival probability of the inital state in system-II with the basis set representation. Continuous line: Exact calculation. Dashed line: Normally ordered MRTDCCM at S^1 level. Dash and dotted line: Ordinary MRTDCCM with S^1 approximation.

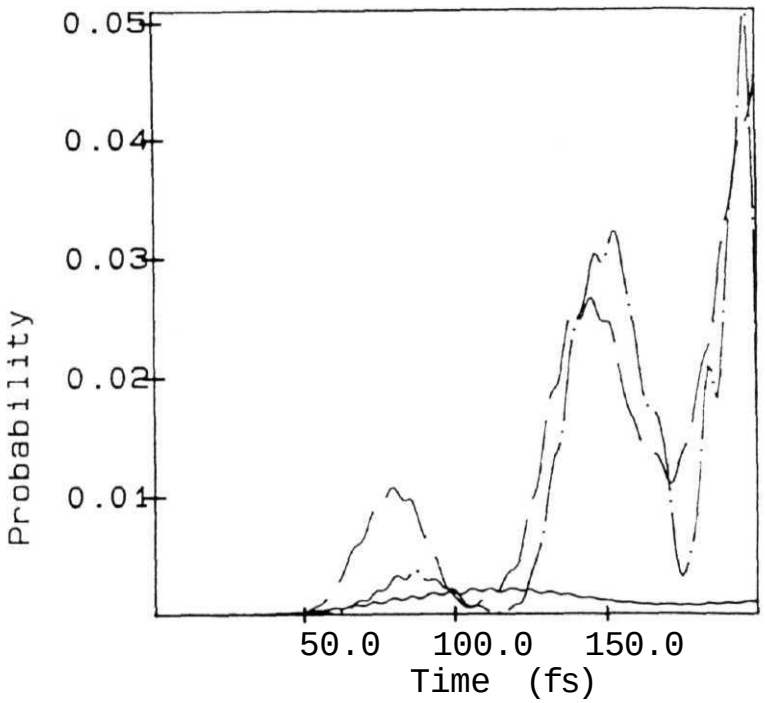

Fig.4.14 The survival probability of the final state in system-II in the basis set representation. The figure conventions are the same as in Fig. 4.13.

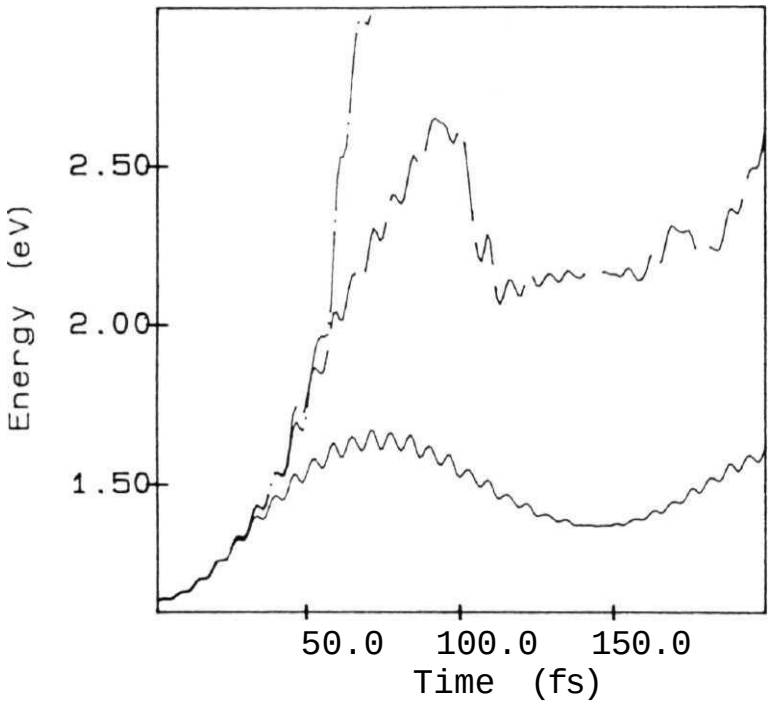

Fig.4.15 The energy of the Morse mode in system-II in the basis set representation. The figure conventions are the same as in Fig.4.13.

function of time obtained using ordinary MRTDCCM and the normally ordered MRTDCCM for this system. Both the calculations provide a very good description of the decay of the probability and are in good agreement with the exact calculation up to about 100 fs. In contrast to the results of system-I the normally ordered version provided equally good convergence for this system. The probability of the final state plotted in the Fig.4.14 also showed similar trends.

In Fig.4.15 we plot the energy of the Morse mode as a function of time for this system computed in the ordinary and the normally ordered versions of MRTDCCM at S = S^1 approximation. Both the calculations provided converged values of energy up to 40 fs. After 40 fs both the calculations deviate from the exact calculation but the ordinary MRTDCCM deviates more because of the norm violation effects which are inherent for this formalism.

4.4. Concluding Remarks

In the application of MRTDCCM approach where the basis set representation is used for the system-I, for the initial conditions that we have studied, only a very small part of the wave packet resides within the model space by about 3 to 4 vibrational periods and there are no significant recurrences up to about 10 vibrational periods. This rapid and irreversible decay is due to the presence of several overlapping nonlinear resonances. All these resonances involve only two modes at a time i.e., the CH mode and one of the bath modes. With respect to the model space however, they appear as multi-mode resonances. Thus a CI based approach requires the inclusion of multi mode excitation

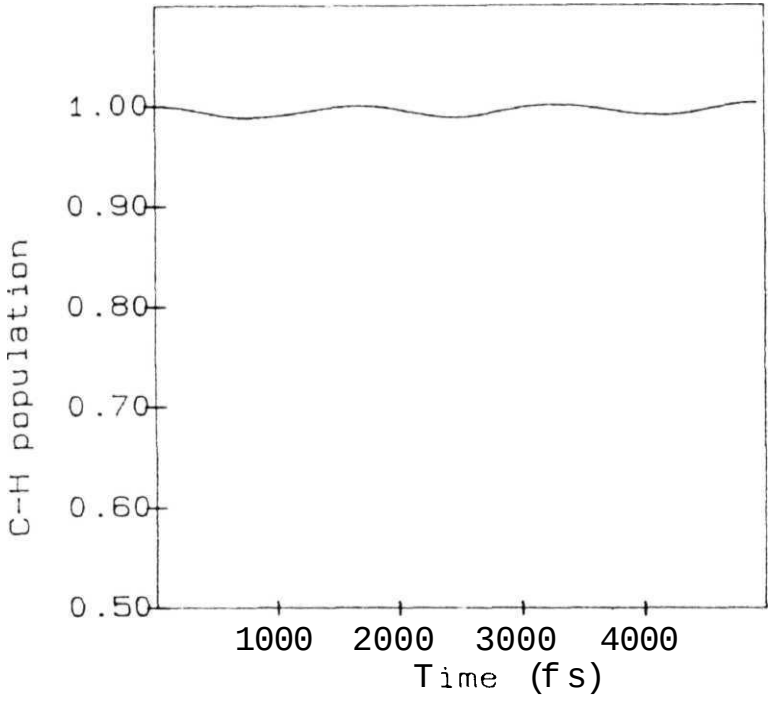

Fig.4.16 The C-H chromophore population in CD_3H by TDSCF. The initial state was 6ν .

operators in U for converged results. The MRTDCCM approach with ordinary exp(S) ansatz is able to provide an adequate description of IVR at two body level even in this case since it simulates the 3, 4 body excitations as products of S^1 operator. Beyond about 4 vibrational periods the inherent weakness of the method i.e. the development of the intruder states with the complex eigenvalues mars its performance. If the model space is chosen judiciously so as to include all the strongly interacting states, its performance is expected to improve. The ideal model space should contain all the degenerate and quasi-degenerate modes. For example, in a recent study of IVR in CD H it was found that the initially excited CH stretch correlates strongly with doubly degenerate *v* mode due to 2:1 Fermi resonance. We have carried out a TDSCF study of the chromophore population for this system (Fig.4.16). The chromophore population decays slowly during the first few hundreds of femto seconds for this system, while TDSCF does not show any such decay, because of its inability to handle nonlinear resonances. Iung and Leforestier found that major contribution to this comes from only first and fifth modes. Thus if the model space is chosen to contain all possible configurations of these two modes we expect an MRTDCCM approach would provide a good description of over all dynamics of the system. Similarly, in a recent study Wyatt and coworkers[4] found that the dynamics of 21 mode benzene model system is well reproduced by reduced mode (4 or 5 active modes) quantum models, with the rest of the modes interacting weakly. Again a model space chosen to span all the active modes and the effect of the rest of modes being accounted by the wave operator should provide a quantitative description of the system.

The normally ordered exp(S) ansatz does not suffer from the intruder state problem. However, since it is equivalent to a limited basis set theory, it is clearly not converged in the basis and would require the inclusion of higher rank operators just as in CI. The mixed representation reproduced the survival probabilities very well for longer times than the basis set representation, because it effectively includes the full basis of the harmonic oscillator modes.

In the second system within the time scale of our study the many body interactions are not playing major role and so the ordinary MRTDCCM is not producing improved results over the normally ordered MRTDCCM.

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CHAPTER V

A TIME-DEPENDENT COUPLED CLUSTER METHOD STUDY OF NONADIABATIC DYNAMICS

5.1. INTRODUCTION

In the previous chapter we have studied the intramolecular vibrational energy transfer in some model systems using MRTDCCM formalism. In this chapter we study the applicability of TDCCM to study the electronic-vibrational energy transfer in systems containing nonadiabatically coupled potential energy surfaces. The nonadiabatic dynamics on coupled electronic surfaces have attracted much interest recently. "' This is due to the fact that these nonadiabatic effects are associated with many chemically interesting phenomena such as the nonradiative decay of excited electronic states, chemiluminescence in atom - atom and atom - molecule inelastic collision processes etc. The nonadiabatic effects arise when the adiabatic approximation is violated.

In the adiabatic or Born-Oppenheimer approximation the nuclei are considered to be stationary when solving the electronic problem. The electronic wave functions and state energies depend parametrically on the nuclear coordinates. The dynamics of the nuclei are generated by a matrix hamiltonian in which the electronic state energies appear in the diagonal elements and act as the potential energy for the nuclei while the matrix elements of the nuclear kinetic energy operator between different electronic states provide the off diagonal couplings. It is commonly assumed that dynamics of nuclei are confined to a single electronic potential energy surface. This is the crux of the adiabatic approximation. This adiabatic approximation is valid

only when the electronic states are well separated in energy compared to the spacings associated with nuclear energy levels. When the potential energy surfaces of different electronic states are close in energy the residual coupling of the nuclear kinetic energy operator between such states becomes significant. The effects associated with this situation are called as nonadiabatic effects. It is convenient to treat the nonadiabatic effects in diabatic basis.[1,22] In this basis a complete set of electronic wave functions are defined such that the nuclear kinetic energy operator is diagonal in them, however, the electronic hamiltonian is not diagonal in this basis, and thus provides both diagonal and off-diagonal coupling matrix elements to the nuclear matrix hamiltonian. In this basis the matrix hamiltonian for the nuclear motion is written as

$$H = T_N 1 + W(Q), \tag{5.1.1}$$

where T_N is the diagonal kinetic energy operator and $W(Q)$ matrix elements are defined as

$$W_{nm}(Q) = \int dr\, \phi_n^*(r,Q)\, H_e \phi_m(r,Q). \tag{5.1.2}$$

Here $\phi_n(r,Q)$ are diabatic wave functions.

The hamiltonian H in eq.(5.1.1) is an infinite dimensional matrix operator. In most situations only a few electronic states interact strongly. Consequently only such states are included and a finite dimensional matrix operator is used to approximate H. For studies of spectroscopic interest,

further approximations are made. For example expanding W(Q) as a Taylor series around the ground surface equilibrium geometry and truncating after linear term in Q, results in the linear coupling model. In this model the terms in the hamiltonian matrix elements are

$$H_{nn} = T_N + + E_n + \sum_S k_S^{(n)} Q_S + 1/2 \sum_{RS} V_{RS} Q_R Q_S, \qquad (5.1.3a)$$

$$H_{nm} = \lambda_0^{(n,m)} \sum_S \lambda_S^{(n,m)} Q_S. \qquad (5.1.3b)$$

Here the energies E_n are constants and are given by $W_{nn}(Q)$. $k_5^{(n)}$ are intrastate electronic-vibrational energy coupling constants and $X^{n,'}$ are interstate coupling constants. In general these coupling constants are determined by ab initio methods. Generally totally symmetric normal modes give rise to nonzero intrastate coupling constants and the nontotally symmetric modes to nonzero interstate coupling constants. The totally symmetric modes modulate the energy separation between the electronic states and are termed as tuning modes and the nontotally symmetric modes are termed as coupling modes.

The use of diabatic basis is particularly advantageous when the potential energy surfaces of the concerned electronic states become degenerate in the n-dimensional normal coordinate space forming a conical intersection.[1,23] The main reason for this is the complicated behaviour of the matrix elements of nonadiabatic coupling operators in the vicinity of avoided crossings. These elements are principally singular at the

point of intersection and show rapid oscillations near it and thus are difficult to handle numerically.[22,23] On the other hand the coupling matrix elements are well behaved in the diabatic basis and can often be modeled in terms of simple functions of nuclear coordinates. The linear coupling model defined above is an example of such simple parametrization and is quite successful in providing interpretation for several spectroscopic studies.

The standard theoretical method to obtain the nonadiabatic dynamics is the time-independent approach based on the Ritz-variational principle. In this method one constructs the hamiltonian matrix in a basis formed by the product functions of electronic and vibrational states of the uncoupled system. This hamiltonian matrix is then diagonalised to give the eigen values and eigenvectors. The required physical quantities are then determined from these. The computational requirement for the diagonalization procedure goes as N, where N is the dimension of the hamiltonian matrix. Moreover the number of basis functions needed to treat a coupled d degree of freedom problem is proportional to M, where M is the number of basis functions for a typical one degree of freedom problem. A more efficient procedure is to directly integrate the TDSE in the zeroth order basis without prediagonalising the hamiltonian. Since this involve multiplication of the wave function with the hamiltonian matrix at each step, the computational effort scale proportional to N^2. In addition the hamiltonian matrix of the nonadiabatic problems are often quite sparse. Utilizing this the matrix multiplication can be reduced to 0(N) process. Several authors have reported such

dynamical calculations.[1"7] Though these methods are dependable the basic problem is that the size of the Hilbert space scales exponentially as M^d thus making it difficult to study systems with more than four degrees of freedom. Alternative methods developed for the problem are time-dependent perturbative approach,[8,9] semiclassical methods, the time-dependent self consistent field (TDSCF) method[13] and the path integral methods[18,19] etc.. The time-dependent perturbation theory separates the electronic hamiltonian into an uncoupled hamiltonian H and the perturbation V and develops power series expansion for the evolution operator in terms of the nonadiabatic coupling constant. Coalson and Kinsey[8] have applied this method to a two state one vibrational mode model system and concluded that it breaks down in the strong coupling limit and for the long time dynamics.

Meyer and Miller[10] have developed a classical analog for electronic degrees of freedom. In this method one constructs the electronic hamiltonian matrix formed by the electronic states whose elements depend on the nuclear coordinates. The equations for the electronic motion are obtained by solving the TDSE where the nuclear coordinates are taken to be time-dependent and the nuclear motion is treated classically. This method is computationally simple to implement. Meyer[10] used it to calculate the nonradiative decay rates in C_2H_4 cation. Zwanziger et al.[11] performed a semiclassical quantization of classical analog model. Application of this method to E®e Jahn-Teller problem in the region of linear coupling provided results in good agreement with

exact quantum mechanical solution. Recently Stock and Miller[12] developed a classical model based on the Meyer and Miller[10] framework of the classical electron analog model for the determination of nonadiabatic excited state dynamics. The method is tested for the four-mode model of the S_2-S_1 intersection in pyrazine and on 3 state, 5-mode and 5-state, 16-mode models of benzene cation. This method reproduces the qualitative features of time and frequency resolved absorption spectra as in the exact quantum mechanical calculation.

The TDSCF method[13-17] has been used by few authors to study the nonadiabatic dynamics. The computational effort in this approach scales linearly with the number of vibrational modes. As the TDSCF method does not account for the correlations between the modes it is not dependable in the long time limit and is reliable only for the short time dynamics where the correlation effects are negligible.

Another approach which is used in determining the nonadiabatic dynamics is the path-integral formulation. Coalson used the path-integral framework for spin-boson model problem and found that the spectroscopic observations can be obtained even in the strong coupling regimes using this formulation. A rigorous path-integral approach for determining the nonadiabatic dynamics of the linear coupling model was recently developed by Domcke and co workers. The time-dependent correlation functions are expressed as sums over all possible paths and for each electronic path the multi-mode vibrational propagator factorizes into a product of single-mode propagators. The summation over paths is

replaced by summation over classes as a practical approximation. The propagator averages are calculated by recursive scheme. The calculations they have presented are for four-mode and twenty four-mode pyrazine models. In this method the numerical effort rises only moderately with the number of modes and so is useful for studying the many-mode systems.

These studies provided some qualitative aspects of the results of the nonadiabatic effects in the systems having conically intersecting potential energy surfaces. In these systems the electronic dynamics in a femtosecond time scale are driven by the velocity of the coherent motion in the tuning modes. This dependence induces a slower vibrational dephasing process which destroys the coherence of vibrational motion. When this dephasing is completed the electronic populations are trapped on the lower surface and the electronic decay becomes irreversible.

Recently Sastry et al.[20] ' studied the dynamics of the linear coupling model using time-dependent coupled cluster method. In this study, a mixed representation was used in which all the normal modes were represented by boson ladder operators, while the electronic degree of freedom subsystem was represented in a basis set in a manner very similar to the mixed representation we used for the IVR of system-I in Chapter IV. All states in which the vibrational mode states were v=0 states were included in the model space. The method is quite good for short time dynamics and yields qualitatively correct spectra even when the cluster operator is restricted to have no more than one boson creation operator. At longer times however, the working equations became

stiff and can not be integrated.

Since the MRTDCCM approach in the boson operator representation is not able to provide long time dynamics, we wished to see if TDCCM in a basis set representation is able to provide a better representation. It turn out that TDCCM using stationary basis functions also suffers from the same problems that MRTDCCM approach of Sastry. However doing TDCCM in dynamical basis generated by TDSCF procedure eliminates the stiffness of the equations and we could carry out the calculation for long periods. To test the potentiality of the method we have done some model calculations. We present the working equations in sec.5.2 and the model calculations in sec.5.3. In sec.5.4 we have drawn some conclusions on the validity of the approach for the present problem.

5.2. THEORETICAL FRAMEWORK

5.2.1 Model hamiltonian

We model our systems such that only two electronic states belonging to different irreducible representations and n-vibrational modes are relevant for the dynamics. We impose following simplifications on our model. The model hamiltonian is constructed in the diabatic electronic basis. The harmonic approximation is invoked for the diabatic potential energy surfaces and the vibrational frequencies in all the unperturbed surfaces are assumed to be equal. The interstate and the intrastate coupling constants are approximated by linear terms in

the normal coordinates. After these simplifications the model hamiltonian for the two state n-mode system can be written as

$$H = \sum |e_i\rangle (\varepsilon_i + H_i) \langle e_i| + V_c \qquad \textbf{(5.2.1a)}$$

$$H_i = \sum_n h_{in} = \sum_n (\omega_n (p_n^2 + q_n^2)/2 + k_{in} q_n) \qquad (5.2.1b)$$

$$V_c = |e_i\rangle \sum_c (\lambda_c q_c) \langle e_2| + h.c., \qquad (5.2.1c)$$

where i is the electronic state and n represents the vibrational mode. Here p_n, q_n are the momentum and position operators of the nth vibrational mode, ω_n are the associated frequencies, k_{in} and λ are the intrastate and interstate coupling constants respectively. The modes which contribute to A are called as coupling modes and the modes which contribute to k are tuning modes.

In this nonadiabatic problem the coupling mode and the electronic degrees of freedom interact strongly so we treat them as a single subsystem. The resulting hamiltonian for the system can then be written as

$$H = H^{ec} + H^{t}, \qquad (5.2.2a)$$

$$H^{ec} = \sum_i |e_i\rangle \varepsilon_i \langle e_i| + |e_i\rangle \lambda_c q_c \langle e_2| + \omega_c (p_c^2 + q_c^2)/2 + h.c., \qquad (5.2.2b)$$

$$H^t = \sum_i |e_i\rangle k_{it} q_t \langle e_i| + \sum_t \omega_t (p_t^2 + q_t^2)/2. \qquad (5.2.2c)$$

Here H^{ec} is the hamiltonian corresponding to coupling mode electronic degree subsystem and H is the hamiltonian for the tuning modes. We now define the basis functions required. For the tuning modes we utilize the harmonic oscillator eigenfunctions centered at the origin and their width parameters were chosen to match the frequencies of the ground surface. For the coupling mode electronic degrees subsystem the basis functions are $\{|e\rangle|\phi_{\sim}^c\rangle;\ i=1,2;0 \le n \le \infty\}$. As long as the two electronic states concerned belong to two different irreducible representations, this space can be separated into different symmetry spaces. Depending on the initial conditions (i.e. the electronic surface on which the wave packet starts at t=0) the dynamics would be confined to one or the other subspace. Thus it is sufficient to consider any one of the two subspaces. Note that the harmonic oscillator eigenfunctions with even quantum number are always totally symmetric, while those of the odd quantum number belong to the same irreducible representation as the normal coordinate concerned. Since the coupling coordinate belongs to the direct product symmetry of the two electronic states, the two subspaces have exactly the same number of functions as the harmonic oscillator Hilbert space and thus are labeled by harmonic oscillator quantum numbers alone. The initial conditions then uniquely determine the electronic state associated with each vibrational state. We have used these subspaces in our computations. The diagrammatic notations for the hamiltonian

terms in this basis are presented in Fig.5.1a.

5.2.2. TDCCM ansatz:

We now turn to the parametrization of the time-dependent wave function in the TDCCM framework. The wave function ψ is written as

$$\psi = U\phi_0. \tag{5.2.3}$$

Since we are interested primarily in the spectroscopic properties of the upper surface of the two interacting electronic states, the initial state is the vibration less state of the electronic ground state transported vertically on to the upper surface. Thus we take the CCM reference wave function ϕ to be

$$\phi_0 = \phi_{ec}^{(0)}(r_e, q_c) \prod_t \phi_t^{(0)}(q_t) . \tag{5.2.4}$$

Based on the operator manifold analysis of Chapter III the operator sets for the model problem are identified. Since the model space contains zero valence particles, only C and B type operators sets are necessary for obtaining the dynamics in this model.

$$C_0 = (1)$$
$$B_0 = (a_m^{i+} a_0^i,\ a_m^{i+} a_0^i a_n^{j+} a_0^j, \ldots;\ i,j \in ec \text{ or } t).$$

Here m and n are the basis function indices.

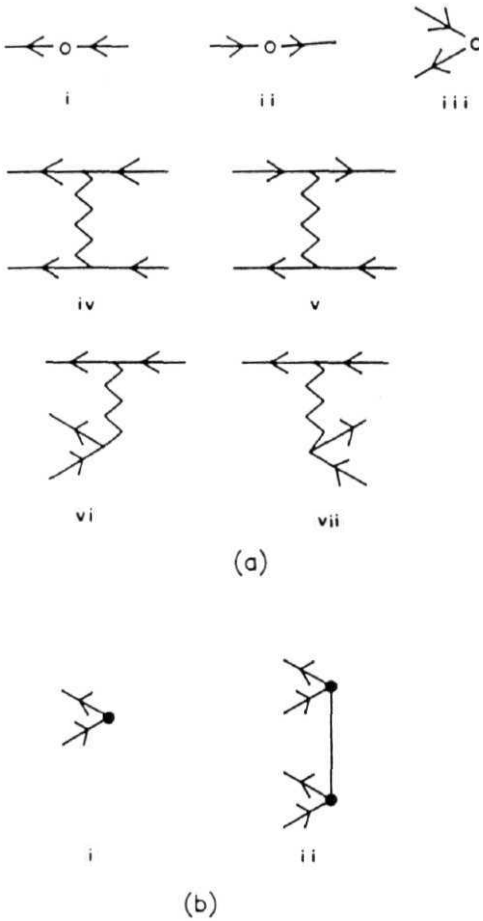

Fig.5.1 (a) The diagrammatic representation of hamiltonian terms. In the diagrams from iv to vii the top line is always ec subsystem mode and it is diagonal. (b) The diagrammatic notations for the cluster operators S_1^-, S_2^-.

The model space evolution operator can then be written as

$$U = U_0. \qquad (5.2.5a)$$

TDCCM[24] posits an exponential form to the evolution operator. U can then be written as

$$U_0 = \exp(S^0);\ S^0 \in C_0 \cup B_0. \qquad (5.2.5b)$$

The cluster operator S° is expanded as

$$S^0 = S_0^0 + S_1^0 + S_2^0 + \ldots \qquad (5.2.5c)$$

$$S_0^0 = s_0^0.1, \qquad (5.2.5d)$$

$$S_1^0 = \sum_{i,m} s_m^i a_m^{i+} a_0^i, \qquad (5.2.5e)$$

$$S_2^0 = \sum_{ij,mn} s_{mn}^{ij} a_m^{i+} a_0^i a_n^{j+} a_0^j \ldots \qquad (5.2.5e)$$

where i,j,m,n are defined as earlier and the subscript 0 indicates the hole state. Some of these are depicted in the **Fig.5.1b.** The working equations are then derived from the equations

$$P(U^{-1}HU - iU^{-1}\dot{U})P = 0 \qquad (5.2.6a)$$

for S_0^0 and

$$Q(U^{-1}HU - iU^{-1}\dot{U})P = 0 \qquad (5.2.6b)$$

for S°. Derivation of the working equations is once again carried out in the diagrammatic notation and the resulting equations for $i\dot{S}^0$, $i\dot{S}^0$ and $i\dot{S}^0$ are presented in Fig.5.2a, Fig.5.2b and Fig.5.2c respectively. These differential equations are integrated using fourth order Runge-Kutta scheme. The equations became stiff in a very short period of time and we could not get enough information to obtain the sufficiently resolved spectra. In view of the failure of this single reference TDCCM the other alternative that strikes is the MRTDCCM formalism.

As discussed in the previous chapter the MRTDCCM[25,26] generates all the higher body excitations from the multi-reference initial state. From the work of Madhavi Sastry[20(']' on the same nonadiabatic model problem it was known that the MRTDCCM equations are more flexible than the single reference TDCCM equations but the long time dynamics (beyond 50 fs) can not be obtained even in this formalism.

In these two formalisms the dynamics are obtained by following the evolution of initial state within the TDCCM or MRTDCCM framework but using static basis functions. One problem in using the static basis functions is that the wave packet leaves the model space in exceedingly short time and the nonadiabatic coupling terms are quite large. As a consequence the intruder states with complex eigenvalues become important even in short time dynamics. This problem can be circumvented by using the dynamical basis sets in terms of which the reference state used in TDCCM has significant overlap with the exact wave function over long periods. Over the last few years several authors have

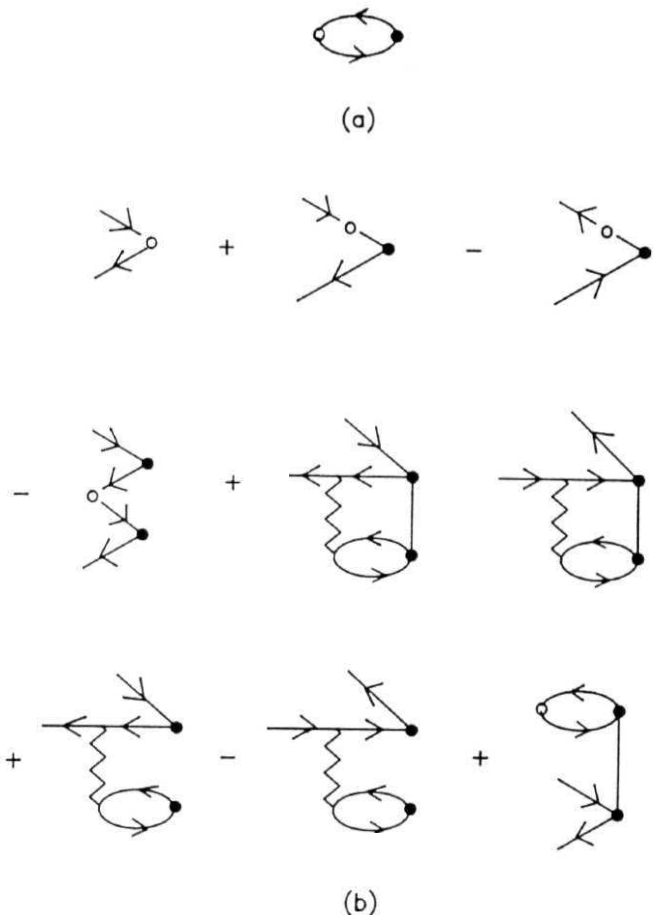

Fig.5.2 Continued

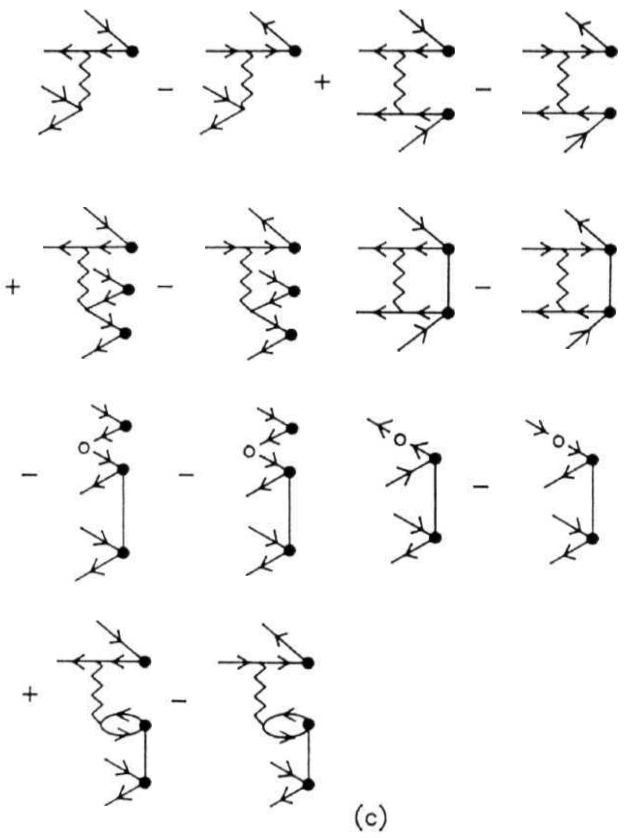

Fig.5.2 The diagrammatic representation of the equations for (a) $i\dot{s}^0$ (b) $i\dot{S}^0$ and (c) $i\dot{s}^0$.

discussed the advantages of these dynamical basis functions. We specifically use the basis functions generated by TDSCF approach for this system. The TDSCF calculations for this problem are already done in our group and from these calculations we knew that it performs quite well up to about 100fs. With this background we have considered the TDSCF calculation to generate a dynamical basis to perform TDCCM calculation. In the following section we obtain the working equations in this formalism.

5.2.3. TDCCM in dynamical basis generated by TDSCF method:

We continue to consider the coupling mode and the electronic degree freedom as a single subsystem. The TDSCF function ϕ is written as

$$\phi^{(t)} = \prod_t \phi_t^{(t)}(q_t)\phi_{ec}^{(t)}(r_e, q_c). \qquad (5.2.7)$$

Here the functions ϕ_t and ϕ are determined by TDSCF method. The working equations for this part are obtained by considering the trial wave function as in eq.(5.2.7) and by employing the Frenkel variational principle $\langle\delta\phi|H - i\partial/\partial t|\phi\rangle = 0$. The equations for ϕ and $<p$ are

$$i\dot{\phi}_t = h_t^{SCF}\phi_t, \qquad (5.2.8a)$$

$$i\dot{\phi}_{ec} = h_{ec}^{SCF}\phi_{ec}, \qquad (5.2.8b)$$

where

$$h_t^{SCF} = \omega_t(p_t^2 + q_t^2)/2 + \sum_i |\langle\phi_{ec}|e_i\rangle|^2 k_{it} q_t, \qquad (5.2.8c)$$

$$h_{ec}^{SCF} = \omega_c(p_c^2 + q_c^2)/2 + \sum_i |e_i\rangle E_i \langle e_i| + V_c, \qquad (5.2.8d)$$

$$E_i = \varepsilon_i + \sum_t \langle\phi_t|(\omega_t(p_t^2 + q_t^2)/2 + \lambda_c q_c|\phi_t\rangle. \qquad (5.2.8e)$$

The TDSCF hamiltonians are then used to generate the dynamical basis functions

$$h_i^{SCF}\phi_i^{(n)} = i\dot{\phi}_i^{(n)}. \qquad (5.2.9)$$

The initial conditions for eq.(5.2.9) are chosen such that all $\phi_\cdot^{(n)}$ are the eigenfunctions of the decoupled oscillators at t=0. Consequently they are orthogonal at t=0 and continue to be orthogonal through out their evolution since h^{SCF} are hermitian operators.

We now invoke the TDCCM ansatz. The SCF solution **for** the **vacuum** state is taken to be the reference state for the **CCM** calculations. As a consequence, the operator space analysis of the previous section is valid here also. However, the single particle creation/annihilation operators are now explicitly time-dependent and obey

$$i\dot{a}_m^{i\,+} = h_i^{SCF} a_m^{i\,+}, \qquad (5.2.10a)$$

$$i\dot{a}_m^{i} = -h_i^{SCF} a_m^{i}. \qquad (5.2.10b)$$

This introduces an additional **term** in the working equations.

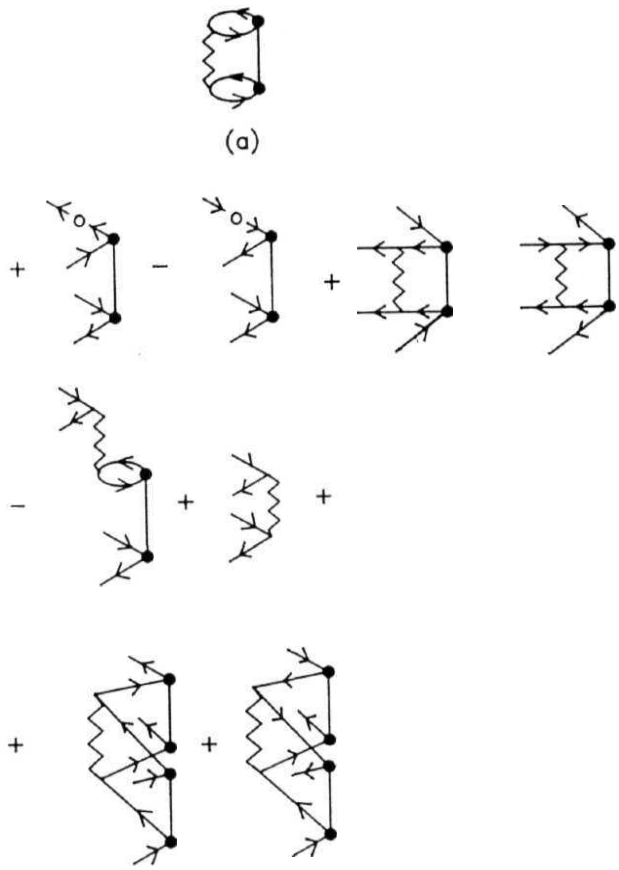

Fig.5.3 The diagrammatic representation of the equations for (a) $i\dot{S}^0$ (b) $i\dot{S}^0$ in the DYTDCCM formalism. Note that the two body vertex is not necessarily diagonal in ec subsystem in the dynamical basis unlike in the stationary basis.

We approximate the one body cluster operator S to zero because the TDSCF method effectively accounts for the one body part of the hamiltonian. Now for the operators S and S we solve the eq. (5.2.6). The diagrammatic representation of the equations for is^0 and is^0 are presented in Fig. 5.3. We have calculated modulus of auto correlation function and the spectra of few model systems. The modulus of auto correlation function represents the probability amplitude that the system after time t is still in the initial state. The spectrum is obtained by Fourier transforming the respective auto correlation functions.

The autocorrelation function is defined as

$$C = \langle \phi_0 | \phi(t) \rangle$$
$$= \langle \phi_0 | \exp(S_0^0 + S_2^0) | \phi_{SCF} \rangle . \qquad (5.2.9a)$$

In our computations we have approximated this to

$$C \approx \langle \phi_0 | \phi_{SCF} \rangle \exp(S_0^0) \qquad (5.2.9b)$$

to avoid the construction of the full wave function exp(S) $|\phi$ >. The model applications and the results are presented in the next section.

5.3. MODEL APPLICATIONS AND RESULTS

Calculations were carried out on four model systems: (1) 3-mode ethylene cation, (2) S_2 surface of 3-mode model

pyrazine, (3) S surface of 4-mode model pyrazine , (4) S_2 surface of 24-mode model pyrazine by TDCCM frame work using the dynamical basis generated by TDSCF and compared with the TDSCF results. We refer our former approach as DYTDCCM from now onwards. The energies of the electronic states, the frequencies and the coupling constants of the vibrational modes we have taken from the literature and are collected in Tab. 5.1.

The parameters k are the intrastate coupling constants and λ is the interstate coupling constant and ω are the corresponding frequencies. c are the energies of lower and upper electronic states.

The results of calculations on the 3-mode ethylene cation are presented in Figs.5.4 and 5.5. In the TDSCF calculations 22 functions were used to represent the coupling mode and the tuning modes were propagated by GWP. As noted in ref.17 the tuning modes experience harmonic potentials in the SCF approximation and so GWP is exact for these. For the coupled cluster calculations 5 of the lowest energy functions were used for each mode.

In Fig.5.4 we have plotted the modulus of autocorrelation function (ACF) against time for the 3-mode ethylene cation calculated in the two formalisms DYTDCCM and TDSCF. For comparison the results of the exact calculations taken from ref.2 are inserted. The initial very fast decay is reproduced by the two formalisms to a very good extent. The amplitude is very small through out its evolution which is generally associated with nonradiative decay process.[35] The ACF

by DYTDCCM is generally smaller than by the TDSCF calculation.

Table 5.1 Parameters used in the model systems:
(All quanitities are in eV.)

el. or vib. mode	lower	upper	ω
ethylene cation (ref.2)			
ε	10.75	12.65	
k_1	0.024	-0.362	0.360
k_2	-0.236	0.330	0.205
λ_c	0.402		0.110
3-mode pyrazine (ref.5)			
ε	3.94	4.84	
k_1	0.037	-0.254	0.126
k_2	-0.105	0.149	0.074
λ_c	0.262		0.118
4-mode pyrazine (ref.19)			
ε	3.94	4.84	
k_1	-0.0964	0.1194	0.0740
k_2	0.0470	0.2012	0.1273
k_3	0.1594	0.0484	0.1568
λ_c	0.1825		0.0936

continued

24-mode pyrazine (19)			
c	3.94	4.84	
k_1	-0.0964	0.1194	0.0740
k_2	0.0470	0.2012	0.1273
k_3	0.1594	0.0484	0.1568
k_4	0.0069	-0.0069	0.0400
k_5	0.0112	-0.0112	0.0589
k_6	0.0102	-0.0102	0.0778
k_7	0.0188	-0.0188	0.0968
k_8	0.0261	-0.0261	0.1157
k_9	0.0308	-0.0308	0.1347
k_{10}	0.0210	-0.0210	0.1536
k_{11}	0.0265	-0.0265	0.1726
k_{12}	0.0196	-0.0196	0.1915
k_{13}	0.0281	-0.0281	0.2105
k_{14}	0.0284	-0.0284	0.2294
k_{15}	0.0361	-0.0361	0.2484
k_{16}	0.0560	-0.0560	0.2673
k_{17}	0.0433	-0.0433	0.2863
k_{18}	0.0625	-0.0625	0.3052
k_{19}	0.0717	-0.0717	0.3242
k_{20}	0.0782	-0.0782	0.3431
k_{21}	0.0780	-0.0780	0.3621
k_{22}	0.0269	-0.0269	0.3810
k_{23}	0.0306	-0.0306	0.4000
λ	0.1825		0.0936

and is closer to the exact calculation of ref.2 (insert a in the Fig.5.4).

Fig.5.5 is the photoelectron spectrum of the ethylene cation second band. The inserts are again from ref.2. Due to the large energy gap of 1.9 eV of the two interacting states the spectral bands are well separated. The gualitative spectrum is reproduced by these two formalisms, but the gross structure of the band is missing in the two formalisms.

In Figs. 5.6 and 5.7 we present the results of the calculations carried out on 3-mode pyrazine. The basis is similar to that used for the ethylene cation. In Fig.5.6 we have plotted the modulus of ACF verses time calculated for S state by DYTDCCM and TDSCF formalisms. The insert is from ref.36. The modulus of ACF is correctly reproduced upto 60 fs by the two formalisms. Beyond this DYTDCCM fails to gain any value and continues to be almost negligible. The underestimation of the modulus of ACF by DYTDCCM is probably due to the term we have neglected in the computation of autocorrelation function. The TDSCF also deviates from the exact calculation, for example around 100 fs the exact calculation fluctuates with the value of 0.1 but the TDSCF shows a sudden rise up to 0.3.

Fig.5.7 is the corresponding absorption spectrum of 3-mode pyrazine upper surface. The inserts are from the calculation of Schneider et al.[5] We can clearly see that the TDSCF spectrum is diffuse and structureless, whereas the DYTDCCM shows the humps which appear in the model exact spectrum (insert b) indicating that DYTDCCM at S_2 level is a better approximation

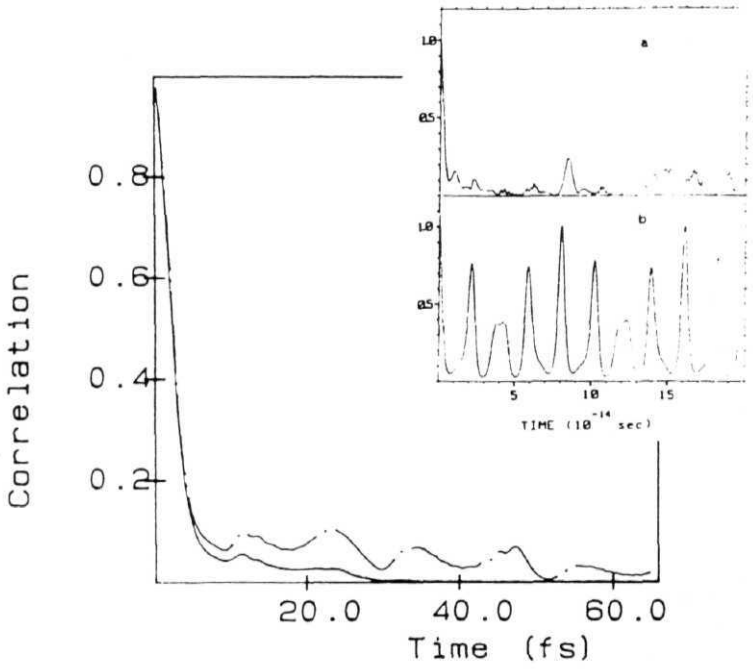

Fig.5.4 The modulus of ACF in 3-mode ethylene cation. Continuous line: DYTDCCM calculation. Dashed line: TDSCF calculation. The insert (a) is the exact calculation and (b) in the absence of vibronic coupling. The inserts are from ref.2.

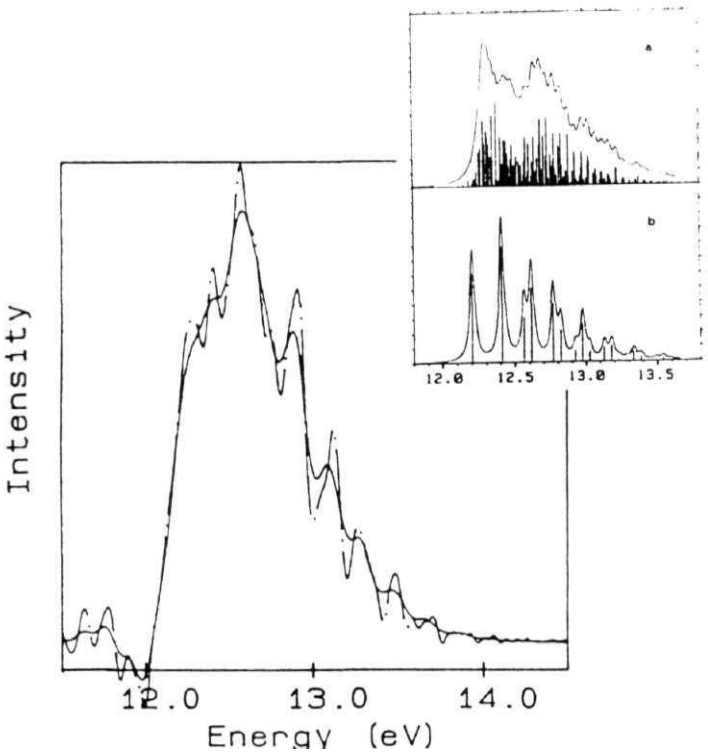

Fig.5.5 The photoelectron spectrum of ethylene cation second band. The figure conventions are the same as in **Fig. 5.4.** The inserts are the corresponding calculations of inserts of **Fig.5.4** taken from ref. 2.

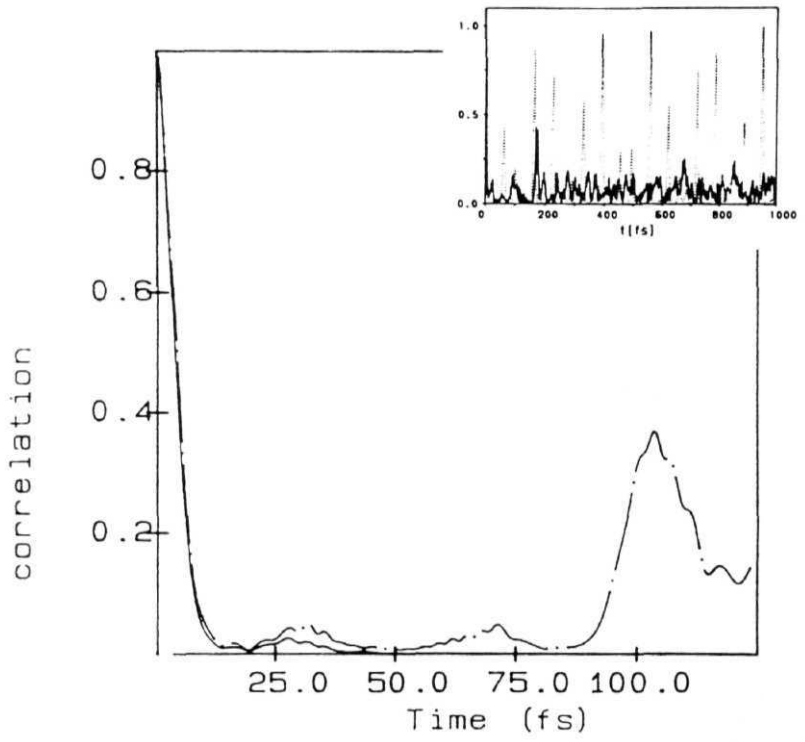

Fig.5.6 The modulus of ACF of S_2 state of 3-mode pyrazine. Continuous line: DYTDCCCM calculation. Dashed line: TDSCF calculation. The insert is form ref.36. Of the two lines of the insert continuous line: the exact calculation and the dashed line: when $\lambda=0$.

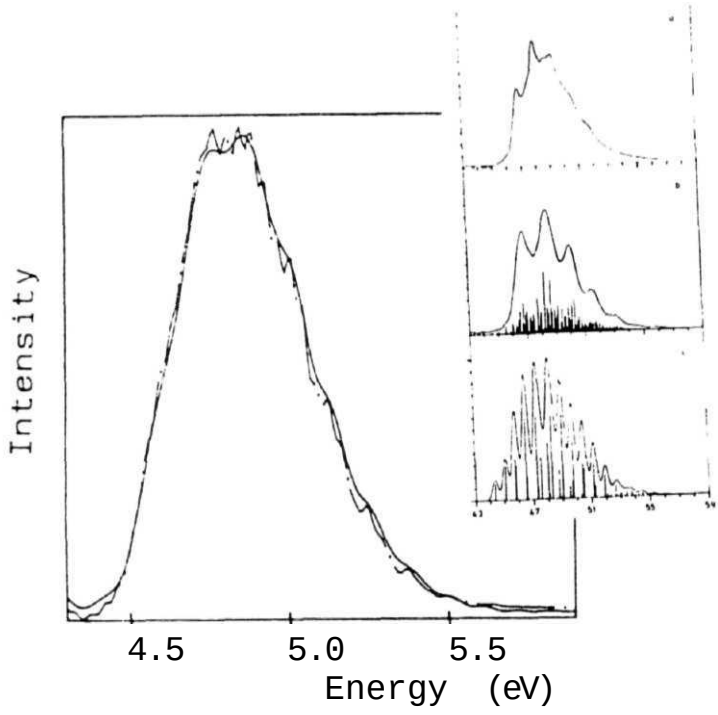

Fig.5.7 The absorption spectrum of S state of 3-mode pyrazine. The figure conventions are the same as in Fig.5.6. The inserts a, b, are the experimental, exact quantum mechanical calculations and c is in the absence of vibronic coupling, $\lambda=0$. The inserts are from ref.5.

than TDSCF.

In Fig.5.8 we plot the modulus of ACF for S_1 state of the 4-mode pyrazine[37] calculated by DYTDCCM and TDSCF formalisms in the same basis as above. Both DYTDCCM and the TDSCF calculations show initial very fast decay and continues to fluctuate with a variable small value through out the evolution. Fig.5.9 is the corresponding absorption spectrum by the two formalisms. The inserts a and b are the exact and the path integral results adapted from ref.19. The TDSCF spectrum is just a broad band while the DYTDCCM calculation produces the qualitative features of the spectrum correctly.

In Figs. 5.10 and 5.11 we present the results of the calculations done for 24-mode pyrazine. The SCF calculation was similar to those reported above. In the TDCCM calculation we have used a smaller basis. The first four modes were represented by 5 SCF functions each as in the previous case and the remaining twenty modes were represented by 2 functions each. In Fig.5.10 we plot the modulus of ACF for S_1 state of 24-mode pyrazine by DYTDCCM and TDSCF calculations. The insert is the path integral calculations taken from ref.19. The initial very fast decay is similar to that in the 4-mode pyrazine in both the calculations. In the long time limit the DYTDCCM result is strongly damped similar to the path-integral calculation.[19] The TDSCF calculation does not show this strong damping. In addition, TDSCF shows strong recurrences at earlier times that are absent in the exact result. The DYTDCCM formalism corrects these anomalous recurrences. Fig.5.11 is the corresponding absorption spectrum of

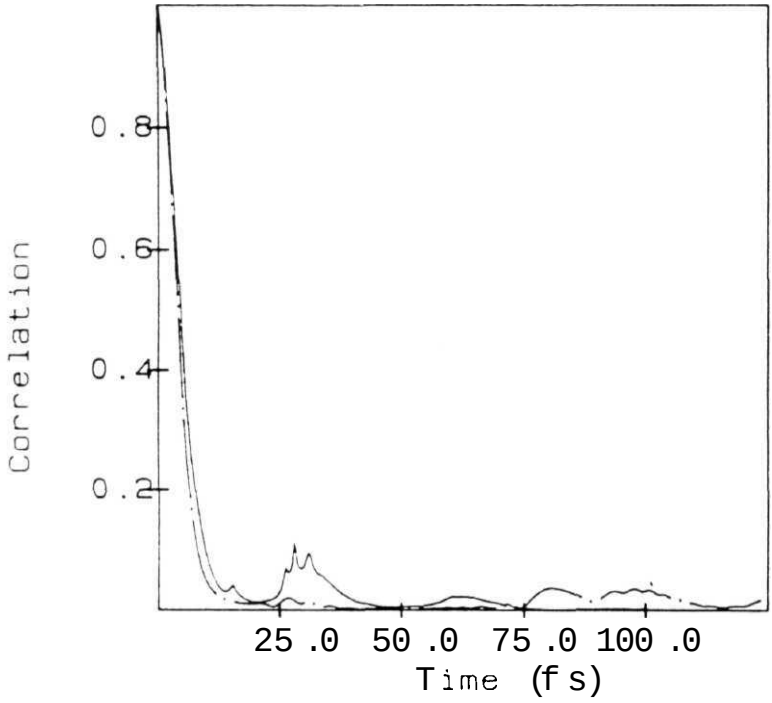

Fig.5.8 The modulus of ACF of S state of 4-mode pyrazine. Continuous line: DYTDCCM calculation. Dashed line: TDSCF calculation.

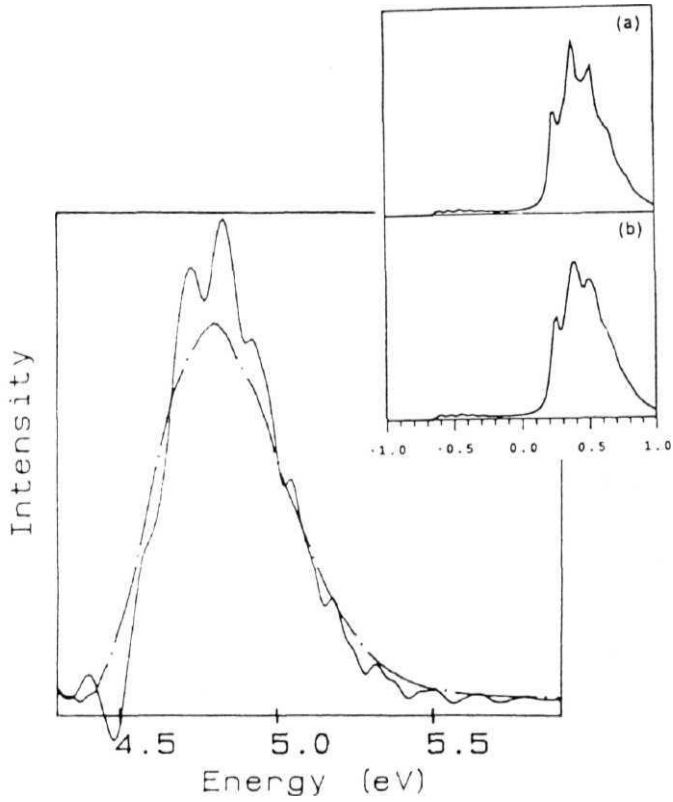

Fig.5.9 The absorption spectrum of S state of 4-mode pyrazine. The figure conventions are the same as in Fig.5.8. The insert a is the exact spectrum and b is the path integral calculation. These are taken from ref.19.

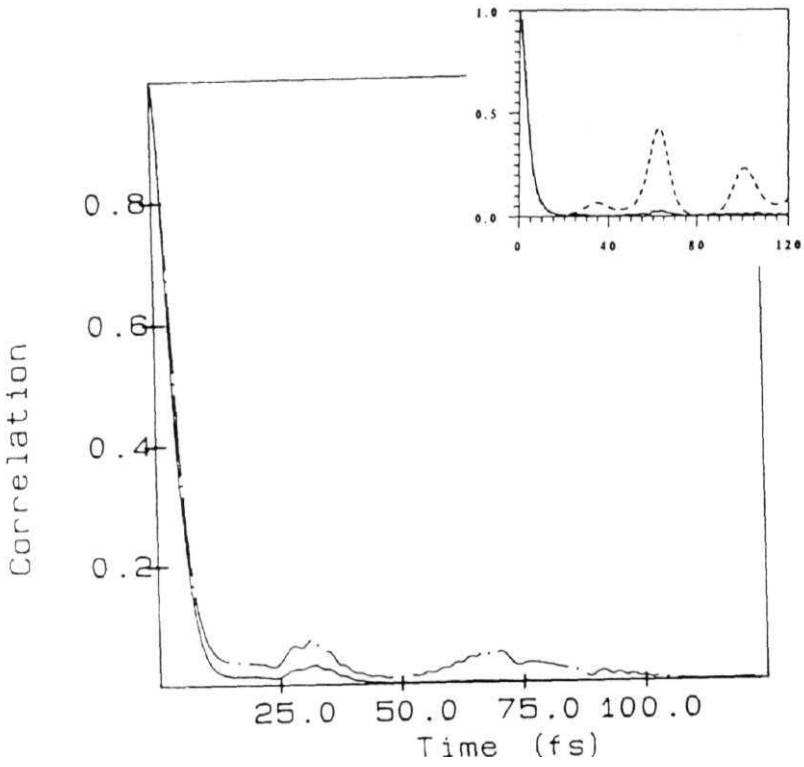

Fig.5.10 The modulus of ACF of S state of 24-mode pyrazine. Continuous line: DY TDCCM calculation. Dashed line: TDSCF calculation. The insert is path-integral calculation (ref.19).

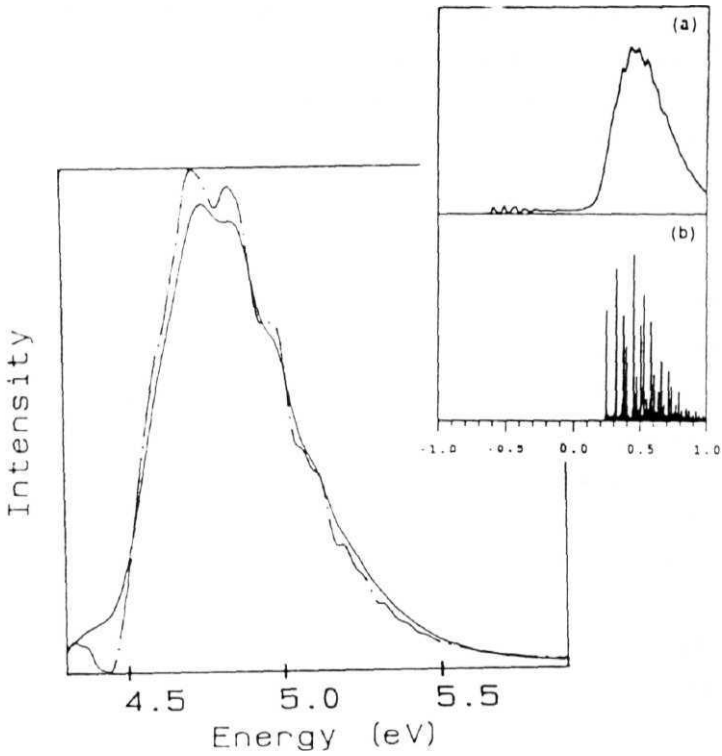

Fig.5.11 The absorption spectrum of S_2 state of 24-mode pyrazine. The figure conventions are the same as in Fig.5.10. The insert is again path-integral calculation (ref.19).

S state of 24-mode pyrazine obtained by DYTDCCM and TDSCF formalisms. Insert a is again the path integral calculation[19] and insert b is the spectrum calculated with X=0 by path integral calculation. The DYTDCCM qualitatively reproduced the spectrum as in the path integral calculation but it differs in the sense that the sharp humps in the path integral calculation are slightly broadened in our calculations.

5.4. CONCLUSIONS

In this chapter we have studied the applicability of TDCCM approach for the description of nonadiabatic dynamics. Our goal was to see whether the TDCCM can provide a qualitatively and quantitatively correct description of the dynamics for this class of systems even with low order truncations. If it can provide such a description, what would be the best basis in which such calculations can be carried out, at what order should the cluster operator be truncated and which configurations should be included in the model space. These systems differ from the system studied in Chapter IV, in that it is known[17] that TDSCF provides a good description for these systems unlike the IVR problem studied there, for which TDSCF gives trivial dynamics. Secondly, there are no dominating resonance sequences in these systems.

To find answers to the questions posed above, we have made two sets of calculations. Since no degeneracies exist in the system, we have assumed that a single reference state would

provide an adequate starting point. In the first approach, we carried out TDCCM calculations in a stationary basis with the initially prepared state as the reference state. The working equations in this approach became stiff very soon and could not be integrated. As noted in Chapter II the working equations became stiff when the overlap of the wave packet with the model space (the reference state in this case) approaches zero. Since the autocorrelation function is practically zero for most of the time in our calculations, this must the reason for the stiffness of the equations. To circumvent this one must choose the model space (the reference function) such that its overlap with the exact wave packet is significant through out the course of its time evolution. Since the TDSCF solution to this class of problems is known to have such acceptable overlap for moderately long times[17], we carried out TDCCM calculation in the dynamical basis generated by TDSCF, i. e. using the TDSCF state of the initial (t=0) state as a reference state. The resulting equations were not stiff indicating that TDSCF does indeed provide a good reference state for the TDCCM calculations.

We next turn to the approximation of the cluster operator. Due to the constraints on computational resources, we could only study one approximation $S \approx S_2$. The computational studies showed that this approximation considerably improved upon the TDSCF results and often is quite close to the exact result.

With these we draw the following tentative conclusions: (1) The TDSCF provides a good reference state for the dynamical calculations, (2) A single reference TDCCM at $S=S_2$ level over this

reference state is adequate to provide a good description for this class of **systems.** More studies are required to confirm these conclusions.

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CHAPTER VI

SUMMARY

In this thesis we were concerned about the development of exponential ansatze for the construction of time evolution operator in the framework of effective hamiltonian theory. We have shown that based on the subalgebraic structure of the spectrum generating algebra under consideration the equations of the time-dependent coefficients belonging to different groups of the generators of the evolution operator are decoupled from each other if a Wei-Norman product form[1] is used with particular groupings of the operators. We then used it to construct perturbation expansions to the wave operator. Three different perturbation schemes are developed: a similarity transformation based perturbation theory (STP), hermitised similarity transformation based theory (HST) and the unitary transformation based perturbation theory (UTP). The HST provides a nonperturbative solution.

The advantage of these perturbation theories is that the working equations for the generators contain finite order polynomials unlike in Magnus expansion.[2] The number of terms at each order of perturbation theory are fewer compared to Magnus expansion. Moreover the conditions under which the solution exists can be laid down. The origin of norm violating intruder states was also analyzed. Some model studies were made to assess the convergence properties of the perturbation theory. In both STP and UTP formalisms the higher order approximations improved upon the lower order perturbation theory. However in STP in the long time limit norm violations are seen due to the intruder state problem. The HST ensures the hermiticity of the underlying effective hamiltonian through out the time evolution and so norm

violations are eliminated in this approach. Unitarised theory (UTP) also eliminate norm violations but this is achieved at the cost of practically eliminating some states from the model space. In general HST performed better. From these conclusions it can be seen that these approaches are useful for the description of dynamics with a large number of strongly interacting states.

We next explored the sub-algebraic structure present in the operator set of the Fock space. There are two reasons for motivating this analysis. This approach provides a pictorial representation of the dynamics of systems in terms of the dynamics of component subsystems. This is because the operators in the Fock space can be classified as one-body, two-body, etc. n-body operators and hence can be identified with the corresponding one-body, two-body, etc. n-body subsystems. In addition, this approach can be used to construct a sequence of nonperturbative approximations in terms of such subsystem amplitudes. We note that in recent years TDSCF approximation had been used with varying degrees of success. The approximations to the evolution operator with one-body operators included in the wave operator is similar (but not identical) to the TDSCF approximation. Thus this approach provides a generalization of TDSCF approach. Inclusion of higher body operators leads to the time-dependent generalization of the multi-reference coupled cluster method (MRTDCCM).

Use of different subalgebra sequences leads to different forms of the wave operator. We have analyzed two such sequences. The first one is essentially the wave operator defined by Mukhopadhyay et al. The other one is the multi-reference

time-dependent generalization of the extended coupled cluster method developed by Arponen.[4] The MRTDCCM approach can be constructed in several representations. We have considered the basis set representation specifically. It is also possible to construct the wave operator in terms of the coordinates and momentum operators of all the particles. This approach was studied by Madhavi Sastry.[5] It is also possible to develop mixed representations in which some degrees of freedom are represented in basis sets while others are represented in terms of their coordinates and momenta.

Given the TDCCM framework the next question we addressed is the utility of such an approximation in dynamics. Specifically we tried to see whether a low body (two body) expansion to the cluster operator is capable of providing a quantitative description of the over all dynamics of various classes of chemically interesting systems. Such studies have been carried out in the electronic structure theories.[6] The two-body nature of the Coulomb interaction and the Pauli's exclusion principle assure us that the two-body expansion of the cluster operator is adequate there. Very few such studies have appeared to date for nonstationary systems.

The first example we have studied is the intramolecular vibrational energy relaxation process in a model hydrocarbon chain. This system consists of several overlapping nonlinear resonances which involve the interaction of many modes. We have taken our model space such that the quantum number of the bath degrees of freedom remain the same in all the states of the model space. This model space has the advantage that it provides a one

to one correspondance with the Morse oscillator states. Moreover all the states that are nearly degenerate with the initial state can be reached by the action of two-body operators on the model space functions. The convergence studies with two-body **and** three-body cluster approximations have proved that the two-body operators provide adequate description of the dynamics.

The dynamics are studied both in the basis set representation and in the mixed representation in which CH Morse mode is treated in the basis set representation and **the** CC harmonic bath modes are represented by boson ladder operators. In **the** basis set representation the ordinary exp(S) results are compared with the normally ordered exp(S) results. The ordinary exp(S) at two body level produced converged results up to 4 vibrational periods whereas the normally ordered results are not converged up to this point. Beyond 4 vibrational periods due to the development of intruder states the performance is effected in the ordinary exp(S) ansatz. If the model space is chosen so as to include all the strongly interacting states the results are expected to improve. The mixed representation reproduced **the** results for longer times than the basis set representation method.

The Next problem we have studied is the nonadiabatic dynamics in the framework of linear coupling model.[8] The initial state was used as the reference for a single reference TDCCM calculation. The working equations for the cluster operators in this approach became stiff within a very short period of time. This is because the ACF becomes practically zero by this stage. One way of overcoming this would be to use a dynamical basis set such that the reference function used for TDCCM in that basis has

a large overlap with the exact wave packet. We used the TDSCF solution to the problem as the reference function as TDSCF is known to provide reasonably good description upto about 100fs.[9] The modulus of autocorrelation function and the spectra are computed for four model systems and compared with the TDSCF calculation. In all these cases we found that TDCCM performed better than the TDSCF.

On the whole we believe that the computational evidence provided here is indicative of the potential of the TDCCM approach. If the model space is judiciously chosen we believe it can offer quantitative description even at two-body approximation to the cluster operator. These conclusions are ofcourse tentative and would have to be tested on wider range of problems and more realistic potential energy surfaces.

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List of publications

1. 'On the development of exponential ansatze for quantum dynamics in finite dimensional vector spaces'; G. Sree Latha and M. Durga Prasad, Theor. Chim. Acta, 86, 511 (1993).
2. 'Lie-algebraic structure and coupled cluster method'; G. Sree Latha and M. Durga Prasad in "Strongly Correlated Systems in Chemistry: Experiment and Theory", S. Ramasesha and D. D. Sarma ed., Narosa.(in press).
3. 'A multi-referencec time-dependent coupled cluster study of intramolecular vibrational relaxation process'; G. Sree Latha and M. Durga Prasad, Chem. Phys. Lett. (submitted).
4. 'Time-dependent coupled cluster method in TDSCF basis: Study of nonadiabatic dynamics'; G. Sree Latha and M. Durga Prasad (Manuscript under preparation).